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ELECTROPHORETIC STUDIES OF WOOL

By Arnold M. Sookne and Milton Harris [1]

ABSTRACT

A new investigation of the electrophoretic properties of wool shows that phthalate ion, used in buffers in earlier work, exhibits a specific ion effect, and shifts the isoelectric point to lower pH values. In acetate buffers, the isoelectric point of wool scales and cortical cells was found to be at pH 4.5. Samples of ground or powdered wool show an isoelectric point at pH 4.2. Much of the confusion which exists concerning the location of the isoelectric point has arisen from the assumption that the isoionic and isoelectric points are identical. The significance of both of these points in wool processing is discussed.

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I. INTRODUCTION

Electrophoretic measurements have been used for distinguishing protein surfaces [1, 2, 3],[2] and for determining one of the characteristic constants of a protein, namely, the isoelectric point.

Considerable disagreement appears to exist concerning the pH at which wool is isoelectric and the significance of the isoelectric point in wool processing. The chief difficulty arises from the fact that some of the values have been determined by methods which do not necessarily define isoelectric points. In the present paper an attempt is made to clarify this situation. In addition, the results of a new investigation of the electrophoretic properties of wool are presented.

As defined by Abramson [1], the isoelectric state of a surface is that electrical state in which the sum of the positive and negative charges at the surface over a time average is equal to zero. The *isoelectric point*, then, is defined as the reference concentration of hydrogen ion or some other ion (Th^{++++}, for example) at which this condition is found; that is, the condition at which the electric mobility is zero. Although it has become customary to define the isoelectric point in terms of the pH scale, it must be defined in terms

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation, Inc.
[2] Figures in brackets indicate the literature references at the end of this paper.

which include a complete description of the medium in which no migration takes place.

The *isoionic point* is defined as the point at which dissociable groups of the substance combine equally and only with hydrogen and hydroxyl ions [6]. This is identical with the isoelectric point only when the substance does not combine with ions other than hydrogen or hydroxyl. It follows then that although it may be possible to determine the isoelectric point by several methods, as by titration, provided that the substance combines with only hydrogen or hydroxyl ions, only an electrokinetic method can determine the isoelectric point in every case. The isoionic and isoelectric points of some soluble proteins have been found to be approximately the same. However, in the case of the insoluble materials, especially those which are more or less crystalline in nature, the isoelectric and isoionic points may be far apart. This is true of crystals of even relatively simple substances, such as amino acids [8]. It has been suggested that in addition to the amphoteric properties at the surface, negative ions are also adsorbed at the surface, which results in a shift of the isoelectric point to lower pH values.

Values for the isoelectric point of wool obtained by a number of investigators are reviewed by Speakman and Stott [4] and for that reason need not be given here. The important fact which should be emphasized is that, with the exception of Harris' earlier value [5], practically all of the values were based either directly or indirectly on determinations of the amount of hydrogen or hydroxyl ion bound by the fiber. The assumption was made that the isoelectric state of a substance is dependent only on the state of its dissociable acid and basic groups (its combination with hydrogen or hydroxyl ions)—that the isoionic and isoelectric points are necessarily identical. This probably accounts for the discrepancy pointed out by Speakman and Stott [4] between the figures pH 5 and pH 3.4 for the "isoelectric" point of wool. The former was determined by titration and may therefore be considered as the isoionic point.[3] The latter was determined by electrophoresis and is therefore the isoelectric point in phthalate buffers. (See below for values in acetate buffers.) Speakman [9] explains the low value determined by electrophoresis as being caused by the presence of –NH– groups on the surface of the wool. Although we agree that the low value is due to a surface phenomenon, it is hard to see how the kind of groups Speakman postulates could cause a lowering rather than a raising of the pH value at which the wool is isoelectric.

II. MATERIALS AND METHODS

Studies of the electrophoretic properties of wool are complicated by the fact that the fibers have a complex morphological structure. In the present investigation an attempt was made to study the component parts of the fiber. Measurements were made on cortical cells, scales, and what is assumed to be the intracellular substance. The scales were obtained by passing wool fibers through a Koerner grinder [10]. This machine produces very little cutting action, since the blades are about $\frac{1}{16}$ inch apart. Microscopic examination of

[3] In an investigation now in progress in this laboratory, it has been found that the point at which combination with acid begins is near pH 6.4 [7].

fibers so treated indicated considerable descaling, but the bulk of the fibers appeared to be uncut. Examination of the particles removed from the fibers showed them to be plate-like and about 2 microns in size.

Cortical cells were obtained by retting fibers with bacteria and also from the dust in a carpet wear-testing machine [4] in which the fibers are broken down by mechanical action.

Fibers were also reduced to a convenient particle size by grinding in a laboratory Wiley mill or in a pebble mill. When the former was used, the wool was ground until it passed through a 60-mesh screen. The powder was suspended in water, the larger particles were allowed to settle, and the particles (1 to 5 microns) remaining in the supernatant liquid were used for the measurements. Both methods of grinding destroyed the cell structure and presumably exposed the intracellular substance.

For the measurement of the electric mobility of ground-wool particles, an Abramson horizontal microelectrophoresis cell was employed. The apparatus and methods were essentially the same as those described by Moyer [12]. The apparatus was checked from time to time by measuring the mobility of human erythrocytes in *M*/15 phosphate buffer at pH 7.4 [13]. Either a 20× ocular and 20× objective or a 28× ocular and 40× water-immersion objective were used.

The mobilities of cortical cells of wool were measured in a vertical microelectrophoresis cell similar to that described by Abramson, Moyer, and Voet [14], since the rapid settling of these large particles made the use of the horizontal cell impossible. In the vertical cell the particle settles in the plane of observation and remains in the same electroosmotic level throughout the measurement. The electric mobility of the particle is the mean of its velocities over a given distance in both directions. The effect of gravitational fall is thus eliminated. When the electric mobility is large compared to the velocity of gravitational fall, the distance traveled in one direction divided by the mean of the times of transit with the current in both directions gives substantially the same result. In extreme cases (for example, in the immediate neighborhood of the isoelectric point) the electric mobility is very small compared to the gravitational fall, and reversal of the current may even fail to reverse the direction of motion of the particle.

Measurements were made in a constant-temperature room at 25° C to avoid convection currents caused by temperature differences. With solutions of ionic strength as low as 0.02 *M*, convection currents were caused by leaving the electric current on for even relatively short periods when the vertical cell was used. For this reason, all measurements in the vertical cell were made in solutions of 0.005 *M* ionic strength, and the current was left on for as short a time as possible. The 20× ocular and 20× objective were used for all measurements in the vertical cell. The cell was checked against the horizontal cell by measuring identical suspensions of wool in both cells. In general, the vertical cell was found more difficult to use and required more

[4] The cells were obtained from a sample of undyed carpet which was subjected to a wear test on the Shawmut carpet-testing machine. The disintegration of fibers under these conditions into cells has been reported by Schiefer and Cleveland [11].

time for a measurement than the horizontal cell, which is well adapted to measurement of the mobilities of small particles.

pH values of the suspensions were measured with a MacInnes and Belcher-type glass electrode and a vacuum-tube potentiometer, using a cathode-ray tube as null indicator. The pH values were referred to potassium acid phthalate, 0.05 *M*, which was assigned a pH value of 4.01 [15].

III. EXPERIMENTS AND DISCUSSION

1. EFFECT OF BUFFERS ON THE ELECTROPHORETIC PROPERTIES OF WOOL

In a recent investigation relating to the electrophoretic properties of silk [16], large ions of complex structure, such as phthalate or picrate, appeared to have specific effects which produced appreciable shifts in the pH-mobility curves. Since phthalate buffers were used in the earlier work by Harris on the isoelectric point of wool, a reinvestigation of the electrophoretic properties of wool fibers was undertaken. The results shown in figure 1 were obtained on wool fibers ground in the laboratory Wiley mill. Curve 3 is the pH-mobility curve for wool in phthalate buffers and shows an isoelectric point at pH 3.4, in agreement with the earlier value of Harris. Curve 1 is a pH-mobility curve for the same sample in acetic acid-sodium acetate buffers of 0.005 *M* ionic strength. Under these conditions the sample is isoelectric at pH 4.2, a shift of approximately 0.8 pH unit. This shift is of the same order of magnitude as that obtained for silk. Curve 2 shows the results for the same sample in acetic acid–sodium acetate buffers of 0.1 *M* ionic strength and shows that the shift in isoelectric point caused by the use of phthalate buffers is not the result of increased ionic strength but has resulted from a specific ion effect.

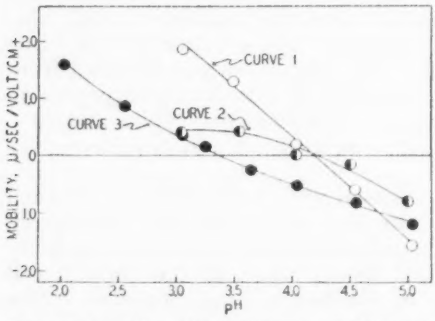

FIGURE 1.—*The electrophoretic mobility in different buffer solutions of wool ground in a Wiley mill.*

Curve 1, 0.005 *M* ionic strength acetic acid-sodium acetate solutions. Curve 2, 0.1 *M* ionic strength acetic acid-sodium acetate solutions. Curve 3, Clark's phthalate buffers.

2. ELECTROPHORETIC PROPERTIES OF CORTICAL CELLS AND SCALES

Figure 2 shows the mobility as a function of pH in 0.005 *M* acetic acid–sodium acetate buffers for three different samples of cortical cells and one sample of scales. One sample of the cells was prepared by the mechanical action of the carpet tester on wool. The other samples were prepared by retting the fibers with bacteria for periods of 4 and 14 months. The scales were obtained by subjecting wool fibers to the action of a Koerner grinder, as previously described.

The results, as shown by the curves, indicate that all three samples of cortical cells and the sample of scales have the same electrophoretic properties and are isoelectric at pH 4.5 in the buffer system used. It

has been suggested by many investigators that an intercellular phase exists between the cortical cells and is removed during prolonged treatment of fibers with certain reagents, such as concentrated ammonia [17], or during retting [18]. If it is assumed that all such material would be removed during the long retting process, but that the cells obtained by mechanical action would still contain some of it, then the only conclusion which may be drawn from the present investigation is that if such a phase exists, it necessarily has the same electrophoretic properties as the outer surface of the cortical cells. Alternative conclusions that the intercellular phase is not completely removed during these treatments or that one does not exist are obviously not eliminated by these results.

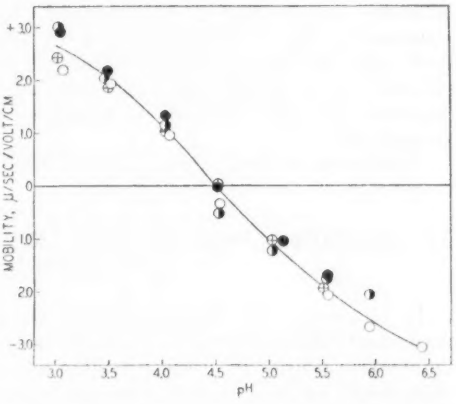

FIGURE 2.—*A comparison of the pH-mobility curves of wool scales and three different samples of cortical cells in acetic acid—sodium acetate solutions of 0.005 M ionic strength.*

Scales prepared by grinding wool in Koerner machine, ⊕; cortical cells obtained by retting wool with bacteria for 4 months, ◑, and for 14 months, ●; and cortical cells prepared by grinding wool in a carpet-testing machine, ○.

3. ELECTROPHORETIC PROPERTIES OF GROUND AND POWDERED WOOL

Figure 3 shows the pH-mobility curve for samples ground in a laboratory Wiley mill and in a ball mill. The dotted curve is the curve taken from figure 2. It has been shown elsewhere [19] and in this laboratory that the action of the ball mill results in a lowering of the cystine content of wool, which suggests that the shift in the curve to lower pH values may have resulted from such degradation. It would appear, however, that the action of the Wiley mill is much less drastic. When fibers were ground in this mill and tested without separation into sizes, no degradation was found. However, this cannot be regarded as proof that the smaller particles were not degraded. The proportion of fine particles is small, so that even if they were highly degraded, it is probable that the effect on the entire mass would not be measurable.

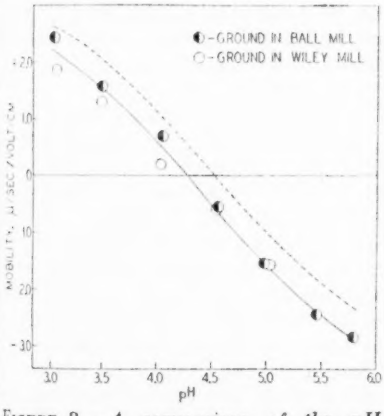

FIGURE 3.—*A comparison of the pH-mobility curves in 0.005 M ionic strength acetic acid–sodium acetate buffers of wool ground in ball mill and Wiley mill.*

The broken line, identical with the smooth curve of figure 2, is included for comparison.

Another explanation for the shift of the curve is that the cortical

cells may be ruptured by the grinding with consequent exposure of an intracellular substance. Since the curve in figure 3 shows the electrophoretic properties of a composite of scales, cells, and intracellular substance, the isoelectric point of the last substance alone would probably be lower than that shown by the curve. This may be considered as a purely physical degradation rather than the chemical degradation (lowering of the cystine content) noted in the preceding paragraph.

Further work is needed to show which, if either, of these explanations is correct.

IV. SIGNIFICANCE OF THE ISOELECTRIC AND ISOIONIC POINTS

It has generally been assumed that the isoelectric point of wool represents the point of maximum stability of the fiber. Although the isoelectric points of some proteins appear to be close to the points of maximum stability, they are not necessarily the same. Actually, it is possible for the stability region of a protein to be far from the isoelectric point [20]. Whether the point of maximum stability will be at or near the isoelectric point will depend upon the reactivity of specific linkages in the molecules. For example, assume that a protein containing disulfide linkages from the amino acid cystine has an isoelectric point in the alkaline region as a consequence of a high content of either lysine or arginine. In view of the known instability of disulfides in even weakly alkaline solutions, it is very unlikely that the point of maximum stability of such a substance would be located near its isoelectric point.

The concept of the isoelectric and isoionic points can be utilized in practical wool processing. Since the isoionic point involves only the acidic and basic properties of the fiber, it should be considered in studying such wool processes as are related to these properties. Dyeing with soluble dyes [21], felting, and removal of ash constituents from the fiber are processes that probably fall within this category. In addition, the swelling and tensile properties of wet fibers are a function of the state of their acidic and basic groups [4, 22].

The isoelectric point, on the other hand, is concerned principally with the total net surface charge, and must only be considered in relation to processes involving either the removal or deposition of materials on the surface of the fiber. In other words, it would play an important part in such processes as scouring and finishing. Scouring is facilitated when the charge on a fiber and the charge on the material being removed from the fiber are the same, and therefore tend to repel each other. For example, dirt particles and particles of most inert substances carry negative charges. Obviously, then, such macroscopic particles are best removed from fibers which also have a large net negative charge. Similarly, the deposition of certain finishing materials on fibers or fabrics is best accomplished when the charges on the fibers and material to be deposited are of opposite sign. Although the dyeing problem is undoubtedly more complicated, it is probable that dyeing with colloidal dyes is related to the isoelectric point.

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Washington, August 15, 1939.

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RESEARCH PAPER RP1246

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RADIUM EXPOSURE METER

By Leon F. Curtiss

ABSTRACT

The meter for radium exposure described in this article is a modification of a portable Geiger-Müller counter unit with a range of sensitivity that is suitable for indicating when the tolerance dosage for gamma-ray exposure has been exceeded.

A milliammeter indicates the actual exposure in roentgens per day, and a light and buzzer are energized when the exposure exceeds the equivalent of 0.1 roentgen per day.

This alarm arrangement is particularly important in handling radium, since it reveals at once when the safe limits of exposure have been exceeded. It has been found of help in ascertaining the effectiveness of lead screening arrangements and storage safes. Where large quantities of radium are in constant use, unsafe conditions may frequently pass unnoticed for a considerable time in the absence of some provision for their detection. This device is of great help in training technicians to follow safety procedures by warning them immediately of unsafe conditions, as far as general exposure is concerned.

The device works from a single alternating-current outlet and will operate continuously. It may be transferred readily to any location where a test of exposure is desired.

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I. INTRODUCTION

In all institutions where large quantities of radium are handled, it is difficult to be certain that the general exposure to gamma-radiation is within the tolerance dosage of 0.1 roentgen per day. It is particularly important to be certain of this at locations more or less continuously occupied by technicians. Although charts and tables are available to indicate safe screening at various distances, when radium is being constantly moved about, these safe conditions may unconsciously be exceeded. It is even possible that unsafe conditions once created may persist for a considerable time, unless daily routine inspections are made to ascertain the actual conditions. Such inspections are difficult to make and, since they consume considerable time, are frequently neglected. A device which would reveal at a glance the actual intensity at a given location in terms of roentgens per day would do much to prevent even temporary overexposure at a given station.

A modification of a portable Geiger-Müller counter equipment which is suitable for determining exposure conditions has been developed by the writer and is described below. This device is arranged to give the exposure in terms of roentgens per day and gives an alarm when the intensity exceeds the tolerance dosage. By its use it is possible to protect workers at their regular stations from a general exposure to gamma-radiation in excess of that regarded as safe.[1]

Furthermore, it is an excellent aid in showing technicians immediately when unsafe conditions have arisen from improper storage of radium and is a great aid in creating respect for safety in general. It should be pointed out that a device of this kind does not give warning of temporary local overexposure. Since prevention of local overexposure is a matter of careful routine under suitably arranged and controlled conditions, and only occurs during actual manipulation of the radium, it can be avoided through careful instruction and supervision. General overexposure is more insidious and can affect, without their knowledge, many individuals who are not actually handling radium. It is felt, therefore, that the device described below should help to bring such conditions to light.

II. DESCRIPTION OF CIRCUIT

For general convenience, it was decided to use a circuit which could be energized from a single alternating-current outlet. To take care of fluctuations in line voltage, a self-regulating B supply was used to insure that the plate voltages of the amplifier remained sensibly constant. A modification of the Neher-Harper circuit was used so that relatively high counting rates for the Geiger-Müller counter could be used. The amplified and leveled pulses were rectified and fed into a condenser. The indicating meter reads the voltage on the condenser. This arrangement is a slight modification of the circuit used in equipment designed and built by the writer for the United States Navy.[2]

The details of the circuit are shown in figure 1, which is a schematic drawing of the wiring and parts. The circuit can be arranged in other ways to make it more compact and reduce the number of tubes and other parts. The one shown is that of the experimental model which has been assembled and tested. It is used as a basis for explanation here, since it reveals more directly the functions of the various parts.

The counter, G–M, is connected to a 57 tube, I, to form a Neher-Harper circuit so that high counting rates may be used. The plate of this tube is connected to the high voltage for the counter through the resistor, R_1, and to the wire of the counter in the usual way. The pulses from the first stage are leveled in amplitude by the second 57 tube, II, and are fed into it through condenser C_1. The pulses are then fed through C_2 to the 27 tube, III, where they are rectified and charge condenser C_3. The final tube, IV, is connected in a vacuum-tube voltmeter circuit to read, by means of the meter, M, the voltage on condenser C_3. This condenser is provided with a resistance leak to ground so that for a constant rate of charging condenser C_3 comes to a steady voltage.

[1] At the present time, a general exposure of 0.1 roentgen per day is regarded as safe. See Handbook H23 of National Bureau of Standards, on Radium Protection.

[2] L. F. Curtiss, J. Research NBS **23**, 137 (1937) RP1223.

The plate voltage for the vacuum-tube voltmeter circuit is supplied from a tap on one of the voltage dividers, *VD*, through resistors R_{12}, R_{13}, R_{14} and R_3. A relay, *Z*, is connected between the midpoint of R_{13} and R_{14} and the plate end of resistor R_{12}. The values of these resistors are chosen so that the relay, *Z*, is closed when the plate current in tube IV drops to a definite value. This point is determined from the calibration of the instrument, as described below, and corresponds to a gamma-ray intensity of 0.1 roentgen per day. The lower part of figure 1 is a diagram of the power supply for the amplifier and counter. As shown, the voltage stabilizer composed of the circuits containing

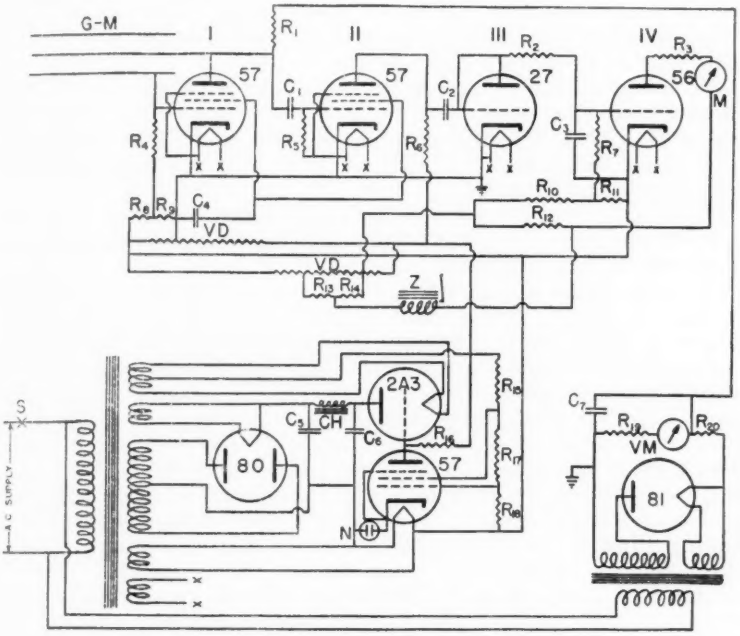

FIGURE 1.—*Wiring diagram of exposure meter.*

R_1, R_4=5 megohms; R_2, R_4=20 megohms; R_3, R_8, R_9, R_{12}=5,000 ohms; R_6, R_{16}=0.5 megohms; R_7=4 megohms; R_{11}, R_{14}=2,000 ohms; R_{10}=0.25 megohms; R_{13}=1,000 ohms; R_{15}=10,000 ohms; R_{17}=27,000 ohms; *N*=*H* neon lamp; *CH* =12 *m h* choke; R_{18}=11,000 ohms; R_{19}=1 megohm; R_{20}=0.1 megohm; C_1=0.0001 *f*; C_2=0.0002 *f*; C_3, C_4, C_5, C_6=8 *f*; C_7=4 *f*; *G-M*=tube counter; *VD*=voltage dividers; *Z*=relay.

the 2A3 and 57 vacuum tubes supplies only the plate voltage for the amplifier. The high voltage from the counter is supplied by a separate transformer and rectifier. A better arrangement would be to take the counter voltage also from the stabilized rectifier. This would eliminate a number of the parts shown and reduce the weight of the instrument. Stabilized high voltage for the counter is not required for counters having a reasonably good plateau.

The circuit can be condensed also by using a single tube having dual electrodes to provide a tetrode and rectifier in the same tube to replace tubes II and III in the amplifier. Such a step is necessary only when space is at a premium, as in portable instruments.

III. THE COUNTER

The intensities to be indicated by the instrument under discussion are in the region of 0.1 roentgen per day, which is a relatively high intensity to measure with a Geiger-Müller counter. It is therefore necessary to use a small counter to obtain the counting rate required, which is of the order of several thousand per minute. This high rate is needed to smooth out statistical fluctuations and give a steady indication on the meter of the instrument for a constant intensity.

By trial, it was found that a counter of the size shown in figure 2 could be used to give a suitable counting rate. By adjusting the size of condensers C_1 and C_2, figure 1, the sensitivity of the apparatus can be controlled within limits, so that there is some latitude in the choice of the sensitivity of the counter itself.

The barrel of the counter is a piece of brass tubing of 1-cm inside diameter and 1 cm long, with walls about 1 mm thick. The central wire is No. 42 AWG steel wire. The counter tube is enclosed in a close-fitting Pyrex tube and filled with an alcohol-argon mixture, as recommended by Trost.[3]

The counter has a plateau extending from 550 to 650 volts and is operated at approximately 600 volts. It is mounted in a tubular brass shield with walls 1 mm thick.

The dimensions chosen for the counter result in several advantages for this particular application. Chief among these is that such a counter is approximately equally sensitive to radiation from all directions. Counters which are longer than their diameter show correspondingly lower sensitivity to radiation in the direction of the axis of the tube. This would be undesirable in the present instrument, since it should respond equally to radiation from any direction. Another advantage is that the counting rate is comparatively low, so that strong sources may be brought near it without resulting in a choking of the Neher-Harper circuit. If a much larger counter were used, the choking effect would render the amplifier inoperative and the meter would fail to register the presence of the radiation. With the counter described, 100 mg of radium in a 2-cm lead cylinder may be brought to within 4 or 5 cm of the counter before any choking of the circuit becomes noticeable. This is a much greater intensity than such an instrument usually would be required to withstand. Finally, the small size of the completed counter tube makes it easy to mount on the amplifier case, so that it is well protected from damage.

IV. ADJUSTMENT AND USE OF THE INSTRUMENT

The parts described above were mounted in a metal cabinet approximately 15 in. high and 7 in. square. The voltmeter of the high-voltage supply and the milliammeter for the vacuum-tube voltmeter were mounted in the sides for convenient observation.

The assembly is shown in figure 3. The buzzer and warning light are actuated by the relay, Z, shown diagramatically in figure 1.

To adjust the instrument, a radium preparation of approximately 1 mg was used. Such a source in glass gives roughly 9 roentgens per hour at a distance of 1 cm, or about 63 roentgens per working day of

[3] A Trost, Z. Physik. **105**, 399 (1937).

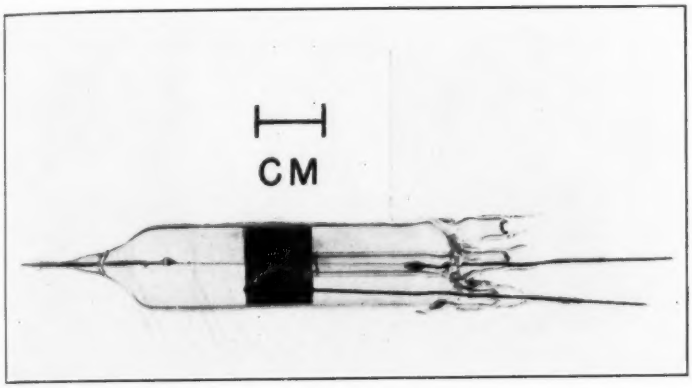

FIGURE 2.—*Tube counter.*

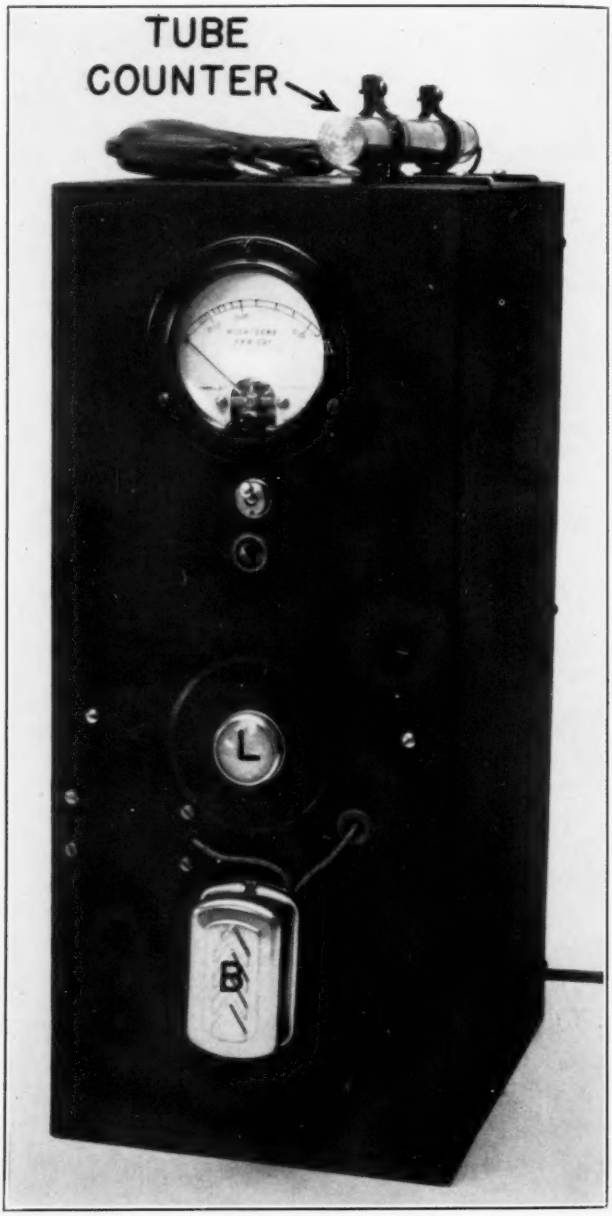

FIGURE 3.—*Completed exposure meter.*

The warning light is shown at *L* and the buzzer at *B*. They are energized when the intensity, as shown on the meter, reaches 0.1 roentgen per day.

7 hours. Therefore, at a distance of 25 cm it would give 0.1 roentgen per day, which is the tolerance dose generally recommended.

With the instrument assembled, the radium source was placed 25 cm from the counter and the sensitivity adjusted by varying the size of the coupling condensers in the amplifier until the steady reading corresponding to 0.1 roentgen per day came just below the linear portion of the operating characteristic of the vacuum-tube voltmeter. The relay circuit was then adjusted, so that the relay would close at this value of the plate current in the vacuum-tube voltmeter.

When the relay closes, a lamp is lighted and a buzzer energized by a separate transformer not shown in the wiring diagram. In this way a direct warning is given whenever the exposure reaches the tolerance level. Approximately 1 minute is required for the instrument to come to a steady reading when the intensity to which it is exposed is suddenly increased from a low value to 0.1 roentgen per day. Therefore, the instrument does not sound a warning when radium is being transported expeditiously through a room or is left

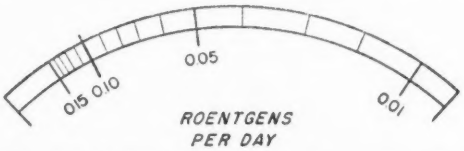

FIGURE 4.—*The scale of the indicating meter showing exposures in terms of roentgens per day.*

unscreened for a brief interval. Consequently, it responds only to exposures which are unduly prolonged in a way to constitute a real hazard.

By varying the distance between the radium source and the counter, a series of readings were obtained for other intensities of exposure. From these readings a new scale was prepared for the meter of the vacuum-tube voltmeter so that it now reads directly in roentgens per day. A sample scale is shown in figure 4. A glance at this meter reveals the actual exposure at any time with reference to the tolerance dose.

In the form described, this equipment provides a portable unit which operates from an alternating-current outlet. It can be placed near any location which is more or less continually occupied by a worker to determine whether exposure conditions are satisfactory and to give warning when the tolerance dose is exceeded. With slight modification, this unit is also suitable for giving warning on a control board in a central office whenever unsafe conditions arise at various locations in an institution. These modified units could be mounted permanently at locations where possibilities of overexposure exist, with the relay circuit connected to lights on the central control board.

The device described has been tested over a period of months in the radium laboratory at the National Bureau of Standards and found reliable in every respect. By its use several unsatisfactory situations which had existed over a considerable period have been brought to light and corrected. The counters, as made at present, have retained their characteristics over a period of a year and presumably can be relied upon for much longer periods.

After proper installation such units require very little attention. They have been found to be helpful in revealing situations where overexposures exist and in training technicians to be careful in handling and storing preparations of radium.

The writer acknowledges the aid of L. L. Stockmann and B. W. Brown in constructing the model of the instrument described.

WASHINGTON, August 4, 1939.

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DETERMINATION OF OPTIMUM VOLTAGE FOR AIRPLANE ELECTRIC SYSTEMS

By Vernon H. Grant[1] and Melville F. Peters

ABSTRACT

The standardization of aircraft equipment is desirable when such standardization does not interfere with efficient operation. The present paper deals with equations which have been developed for the standardization of electric equipment, and which indicate that the voltage for a large number of airplanes using storage batteries to carry peak loads can be advantageously standardized at 24 volts.

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I. INTRODUCTION

Of the multitude of research problems involved in adapting complete electric systems to a basis of minimum weight for a required job, the fundamental problem is that of the characteristics of the power-supply system. At present, direct-current generators in parallel with lead-acid storage batteries provide an acceptable source of electric power in all but the largest airplanes.

The wiring installation of a military or transport airplane consists of insulated copper conductors of various sizes (No. 20 to No. 00 AWG) enclosed in thin-walled rigid or flexible aluminum conduit, with junction boxes, fittings, and other parts forming a complete metal-enclosed system. The remaining equipment, including generators, batteries, motors, lights, solenoids, radio transmitters and receivers, heating units, and other devices is usually constructed according to fundamentally conventional designs and is used in all classes of airplanes.

The earlier types of airplanes carried little electric equipment and the use of 12 volts as standard by the service was satisfactory. With increase in size and the requirement of better performance in all classes of airplanes, there has been a considerable increase in weight of the electric equipment, so that the determination of the optimum voltage, which is the voltage for which the weight of electric equipment is a minimum, has become of paramount importance. Calcu-

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lations were made to determine this optimum voltage. These calculations were long and tedious, since they required a calculation of the weight of the electric system for several voltages. The curve of weight versus voltage based on these calculations indicated that there was a voltage for which the weight was a minimum and that there was a considerable range of voltage over which the weight was very little more than the minimum. This range will be referred to as the minimum region. In making these calculations, certain assumptions had to be made as to the manner in which the weight of the component parts of the system changed with voltage. It was found that by making slight modifications in these assumptions they could be expressed in mathematical form. The analysis which follows shows how the equations used to express these assumptions lead to equations which give the optimum voltage and the minimum region in terms of certain constants associated with the weight of the electric equipment.

Application is made of these equations to existing airplane electric systems to show how their use faciitates the selection of the optimum voltage.

This work was done at the National Bureau of Standards and sponsored by the Bureau of Aeronautics, United States Navy Department.

II. DEVELOPMENT OF EQUATIONS FOR OPTIMUM VOLTAGE

The following treatment of the effect of voltage on the weight of the system is developed after assuming that the weight of the component parts changes with voltage in the following manner:

1. The weights of generators and load equipment (motors, lights, and several other units) are approximately independent of voltage.

2. The weight of a storage battery for a given watt-hour capacity is made up of a constant plus a quantity K_2E, which is a direct function of the number of cells and hence indirectly a function of voltage (see eq 1).

3. The weight of cable and conduit is assumed to be related to the voltage as given in 3A1, 3A2, 3A3; 3B1, 3B2; and 3C1.

3A1. The weight of conductor varies inversely as the square of the voltage except that portion under 3A3.

3A2. The weight of conduit and insulation varies inversely as the voltage over the voltage range considered.

3A3. A certain weight of cable and conduit is independent of the voltage.

3B1. The weight of conductor varies inversely as the square of the voltage.

3B2. The weight of conduit and insulation varies inversely as the voltage.

3C1. The weight of cable and conduit varies inversely as the square of the voltage.

Within the voltage range considered safe for airplane operation, the independence of the weight of generator and load equipment stated with voltage, as under 1, is sufficiently correct for all practical purposes. For lights, switches, fuses, and other small parts, the change in weight with voltage is slight, and in this voltage range the changes may be neglected.

In private communications to the authors, C. B. Mirick, of the Naval Research Laboratory, and H. D. Wilson, of the Auto-Lite Co., have shown that to a close approximation the change in weight of storage batteries of a given type with voltage for a given watt-hour capacity may be represented by eq 1. Their calculations were made for voltages from 6 to 48. In figure 1 are shown changes in weight of storage batteries with voltage for ½- and 1-kw. output for periods of 5 and 20 minutes, respectively. The data were based on batteries now in the service.

The range of K_2 for these batteries is from 0.6 to 0.85. In earlier types of aircraft batteries, K_2 was found to lie between 1.35 and 1 pound per volt, for the outputs shown in figure 1. The latter value

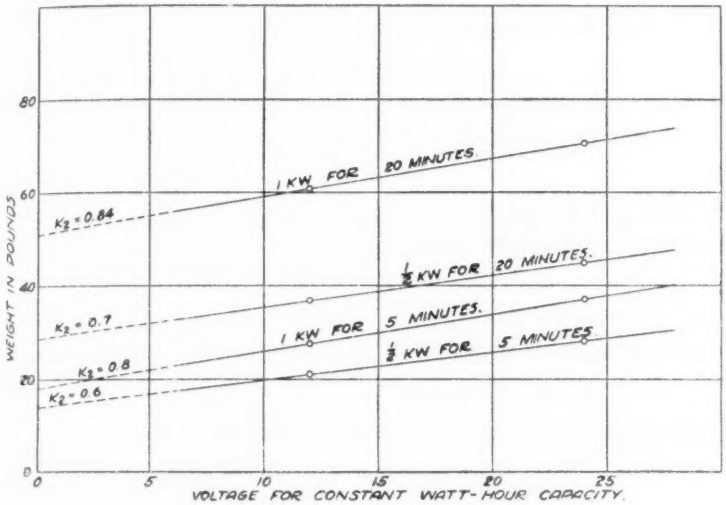

FIGURE 1.

Curves for batteries showing change in weight with voltage for the outputs indicated.

$$W_b = K_a + K_2 E$$

was used in a number of the earlier calculations, and some of the results are given here, using $K_2=1$ instead of $K_2=0.85$.

K_2 changes with the watt-hour capacity of the battery but not with the voltage, and so may be regarded as a constant in subsequent differentiation with respect to voltage.

Assumption 3A1 is strictly true if for each voltage the size of the conductor is selected so as to keep the percentage voltage drop constant.

Assumption 3A2 states that the weight of conduit and insulation changes inversely with the voltage. A more exact equation would indicate the cross-sectional area of the insulation, and the conduit would change with the average radius multiplied by the thickness. Since the thickness of the insulation of the cable does not increase uniformly with the size of the conductor, but with groups of sizes, an equation which would exactly express the relationship between weight of insulation and size of cable is beyond the scope of this inves-

tigation. As will appear later, little difference is obtained in optimum voltage whether this assumption or 3C1 is used.

Assumption 3A3 is made because in many types of airplanes there are low-candlepower lights, indicating devices, and other equipment which require such small currents that mechanical strength limits the size of the conductor rather than the electric resistance.

Assumptions 3B1 and 3B2 are not as close an approximation to the actual relationship between weight and voltage as 3A1, 3A2, 3A3; and 3C1 is not as close as 3B1 and 3B2.

The weight of the electric equipment of any one airplane, according to assumptions 3A1, 3A2, and 3A3, may be stated as follows:

Weight of batteries,

$$W_b = K_0 + K_2 E. \tag{1}$$

Weight of generator, motors, and other parts.

$$W_g = K_1. \tag{2}$$

Weight of conductor, which is larger than the smallest allowable size and therefore changes inversely as the voltage squared,

$$W_w = K_3/E^2. \tag{3}$$

Weight of conduit and insulation, which changes inversely with voltage over the limited voltage range considered,

$$W_c = K_4/E. \tag{4}$$

Weight of cable and conduit, which is of the smallest allowable size and therefore is independent of voltage,

$$W_{wc} = K_5. \tag{5}$$

Adding, the total weight, W, may be written

$$W = K_1 + K_5 + K_0 + K_2 E + \frac{K_3}{E^2} + \frac{K_4}{E}. \tag{6}$$

Strictly speaking, K_5 is not a constant but is a function of voltage, since, if the voltage were very low, all of the conductors might have to be larger than the smallest size having sufficient mechanical strength, whereas if the voltage were sufficiently high, a large proportion of the conductors might be of the smallest practicable size. However, as will be shown later, large changes in the values of K_3 and K_4, within the range of reasonable designs, have little effect on the final result. If K_5 for any one plane does change with voltage, most of the effect of the change is compensated by corresponding changes in K_3 and K_4.

Differentiating eq 6, putting the derivative equal to zero, and solving the resulting equation gives the voltage designated E_0. This voltage will be called the optimum voltage, because it is the voltage for which the system has a minimum weight.

$$\frac{dW}{dE} = K_2 - \frac{2K_3}{E^3} - \frac{K_4}{E^2} = 0 \tag{7}$$

or

$$E_0(K_2 E_0^2 - K_4) = 2K_3, \tag{8}$$

which gives the optimum voltage for assumptions 3A1, 3A2, and 3A3.

If

$$W_{wc}=K_5=0, \tag{9}$$

eq 6 satisfies assumptions 3B1 and 3B2, provided W_w is the total weight of conductor and W_0 the total weight of insulation and conduit The optimum voltage is again given by eq 8, which is written

$$E_0(K_2E_0^2-K_4')=2K_3', \tag{10}$$

the constants K_3 and K_4 being written as K_3' and K_4' to distinguish the assumptions under 3B1 and 3B2.

If $W_{wc}=K_5=0$ and $K_4=0$, this means that the total weight of cable and conduit changes inversely with the voltage squared. This was assumption 3C1 and eq 8 may be written

$$E_0=\left(\frac{2K_3'}{K_2}\right)^{1/3}=A(K_3')^{1/3}, \tag{11}$$

where

$$A=\left(\frac{2}{K_2}\right)^{1/3}.$$

Since W_w in eq 3 now designates the total weight in accordance with assumption 3C1, the constant K_3 is designated by K_3'.

The constant K_1, which designates the weight of the generator, motors, and other parts is of no importance in determining either the shape of the curve or the optimum voltage and in the computations which follow will be omitted. The weight of the system without the generator, motor, lights, and other equipment whose weight is independent of voltage, except that designated by K_5, will be designated W'. Eq 6 may then be written for the weight of battery, cable, and conduit according to assumptions 3A1, 3A2, 3A3; 3B1, 3B2; and C1.

Assumptions 3A1, 3A2, 3A3:

$$W'=K_0+K_2E+\frac{K_3}{E^2}+\frac{K_4}{E}+K_5. \tag{12}$$

Assumptions 3B1 and 3B2:

$$W'=K_0+K_2E+\frac{K_3'}{E^2}+\frac{K_4'}{E}. \tag{13}$$

Assumption 3C1:

$$W'=K_0+K_2E+\frac{K_3'}{E^2}. \tag{14}$$

III. COMPUTATIONS

In table 1 are shown the results of computations for a number of airplanes which, if equipped with 12-volt systems, would require the combined weights of cable and conduit shown in the first column of the table. Columns 2 and 3 of the table show the weights of conductor and conduit and insulation, respectively, on the assumption that 70 percent of the combined weight is that of the conductor. The optimum voltage for each plane, as calculated from eq 11, appears in column 4. In these computations the battery constant, K_2, is taken as 1 for all weights of cable and conduit. If it is assumed that the airplane with the greatest weight of cable and conduit requires the

largest battery, then K_2, if it changes at all, will probably increase with increase in weight of cable and conduit. An inspection of the equations shows that with an increase in K_2 the optimum voltage will be decreased, and if K_2 increases with the size of the plane the optimum voltage for the heavier units will more nearly agree with that for the lighter units than is indicated by the values in table 1. Using the single value $K_2=1$ for all weights of cable and conduit, gives the maximum difference between the optimum voltages for the large and small units.

TABLE 1.—*Optimum voltage for different weights of cables and conduits*

[$K_3=1$]

Weight of cable and conduit of 12-volt system	Weight of conductor	Weight of conduit and insulation	Optimum voltage equation			Increase in weight if 24 volts is used instead of optimum voltage given by eq 11	Increase in weight if 12 volts is used instead of optimum voltage given by eq 11
			11	10	8		
1	2	3	[a] 4	[b] 5	[c] 6	7	8
lb	*lb*	*lb*	*v*	*v*	*v*	*lb*	*lb*
10	7	3	14	13	12.5	5	1
20	14	6	18	18	16	2	5
50	35	15	24	24	22.5	0	25
70	49	21	27	28	25	0	40
100	70	30	30	32	29	3	65
150	105	45	35	37	33	10	110
200	140	60	38	41	37	15	155
300	210	90	44	48	43	30	245
400	280	120	49	54	48	50	340
500	350	150	52.5	59	53	70	435

[a] Column 4, optimum voltage computed from eq 11, $E_0=\left(\frac{2K''_3}{K_3}\right)^{1/2}$, where total weight of cable and conduit for a 12-volt system is taken from column 1.

[b] Column 5, optimum voltage computed from eq 10, $E_0(K_3E^2_0-K'_4)=2K'_3$, where the constants K'_3 and K'_4 are computed from columns 2 and 3, respectively.

[c] Column 6, optimum voltage computed from eq 8, $E_0(K_3E^2_0-K_4)^{2+3}$, where K_3 is obtained by taking 80 percent of the weight of conductor given in column 2 and 70 percent of the weight given in column 3.

The other constant, K''_3, appearing in eq 11 was calculated for each plane from eq 3, using for W_w the combined weight of cable and conduit for a 12-volt system, since, for the conditions under which $K_3=K''_3$, the value of W_w is the combined weight of cable and conduit shown in the first column of table 1.

In column 5 are given the optimum voltages calculated from eq 10. The constants K'_3 and K'_4 appearing in this equation were calculated for each airplane from eq 3 and 4, respectively, using for W_w the values from column 2, and for W_c those from column 3 of table 1, since for the conditions under which $K_3=K'_3$ and $K_4=K'_4$, the value of $K_5=0$.

The optimum voltages in column 6 were calculated from eq 8, with the assumption that the part of the weight which is independent of voltage consists of 20 percent of the weight of conductor and 30 percent of the weight of insulation and conduit in the 12-volt system.

The table indicates that although the assumptions leading to eq 8, 10, and 11 are different, the calculated optimum voltages are nearly the same. The reason for this may be seen by referring to figures 2 and 3. In figure 2 are 10 curves, showing for a number of voltages the total weight of battery, cable, and conduit necessary to replace

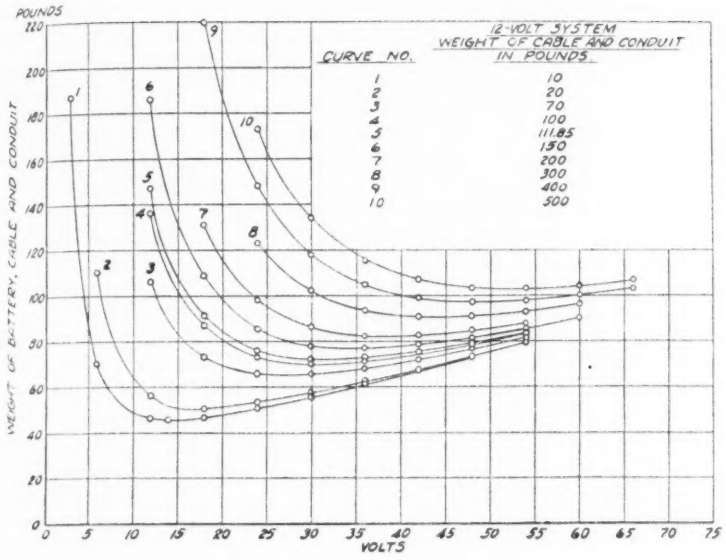

FIGURE 2.

Curves showing the change in weight of battery, cable and conduit with voltage. Values computed from equation 14.

$$W_b = 24 + E.$$

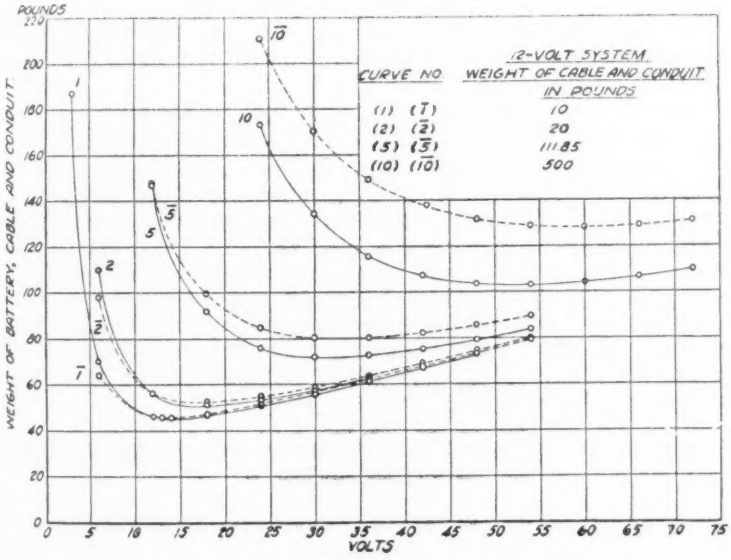

FIGURE 3.

Curves showing the change in weight of battery, cable and conduit with voltage. Values indicated by solid lines are plotted from equation 14. Values indicated by dotted lines are plotted from equation 13.

$$W_b = 24 + E.$$

12-volt systems having weights of cable and conduit ranging from 10 to 500 pounds. These curves are plotted from eq 14. K_2 is taken as unity, and K_0 as 24, which are the values found to satisfy the weight versus voltage relationship for one of the earlier types of batteries. K''_3 is obtained from using for W_w the weights of cable and conduit tabulated on figure 2. The minima on these curves correspond to optimum voltages, and the minimum values are given by eq 11. As the voltage E is increased from zero, each curve rapidly approaches a minimum and then rises slowly. The reason for this may be seen by referring to the equation from which the curves are plotted. In this equation the battery weight K_0+K_2E, increases with the number of cells and hence as the voltage and the weight of the cable and conduit, K''_3/E^2, changes inversely as the second power of the voltage E. Since the constant K_2 is unity, the term K''_3/E^2 is the predominating term for small values of E. As E approaches the optimum voltage, changes in K''_3/E^2 are nearly balanced by changes in K_2E. As E increases, the term K''_3/E^2 becomes less important and as a limiting value the weight, for $K_2=1$, increases approximately 1 pound for each increase in E by 1 volt. For example, if the voltage is decreased from 12 volts to 6 volts, as shown by curve 1 in figure 2, the weight is increased from 46 pounds to 70 pounds, an addition of 24 pounds, whereas increasing the voltage from 12 volts to 24 volts increases the weight to 50 pounds, an increase of only 4 pounds; but a further increase of 12 volts increases the weight 11 pounds. Since the optimum voltage is 14 with a total weight of 45 pounds, increasing the voltage to 24 increases the weight only 5 pounds.

Column 7 of table 1 shows the increase in weight by adopting 24 volts instead of the optimum voltage computed from eq 11. Column 8 shows the increase in weight by adopting 12 volts instead of the optimum voltage. A decided saving in weight is indicated by adopting 24 volts instead of 12 volts.

In figure 3 the curves marked 1, 2, 5, and 10 are reproductions of the corresponding curves of figure 2. The dotted curves $\overline{1}$, $\overline{2}$, $\overline{5}$, and $\overline{10}$ are computed from eq 13. For each curve the values of K'_3 and K'_4 are computed from the weight of conductor and conduit by assuming 70 percent of the weight is conductor and 30 percent of the weight is conduit and insulation. K'_3 is obtained from eq 3 and K'_4 from eq 4, and E is taken as 12 volts for the evaluation. For a total weight of cable and conduit of 10 pound for a 12-volt system the two curves are in agreement, whereas for the corresponding weight of 500 pounds the values given by the two equations differ, but the curves are of the same general shape, and the optimum voltages for one set of curves agree within practical limits with the other.

IV. DETERMINATION OF OPTIMUM VOLTAGE FOR FIVE AIRPLANES

In columns 2, 3, and 4 of table 2 are given the total weights of cable and conduit, the weight of cable and the weight of conduit, respectively, for five different types of airplanes. Since it is difficult to estimate the weight of insulation on the cable, the constant K'_3 is obtained by using the weight of the cable as the weight of the conductor, and K'_4 is calculated from the weight of the conduit. K''_3 is

based on the total weight given in column 2, using eq 3. Substituting these values in eq 10 and 11, with K_2 taken as 0.85, the optimum voltages are obtained. Columns 6 and 7 show the increase in weight if 12 volts is used instead of the optimum voltage. In columns 8 and 9 are given the increases in weight which would result from using 24 volts instead of the optimum voltage. The agreement between these two columns indicates that it is not important whether the optimum voltages are computed from eq 13 or 14 for the range of weights covered by these airplanes. The 10 curves in figure 4 show the change in combined weight of battery, cable, and conduit with voltage, using eq 14 and 13.

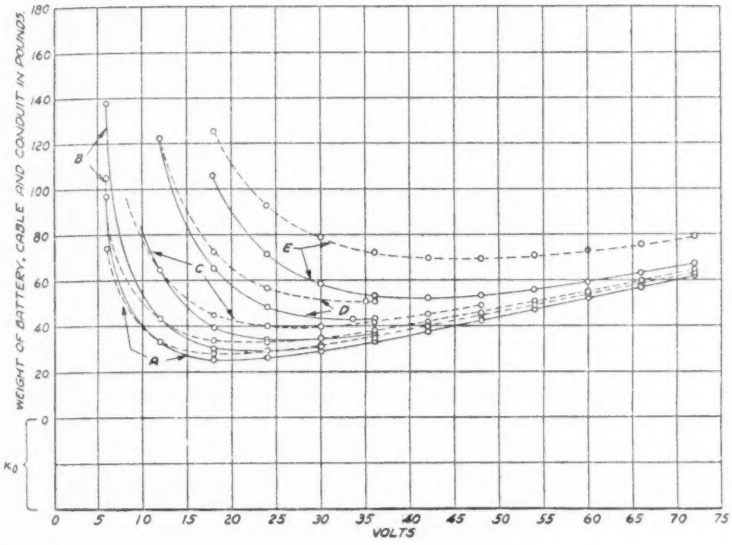

FIGURE 4.

Curves showing the change in weight of equipment with voltage for the five airplanes listed in table 2. Curves with solid lines computed from equation (14). Curves with dotted lines computed from equation (13).

TABLE 2.—*Optimum voltages for five types of airplanes*

Airplane [a]	Weight of cable and conduit for a 12-volt system			Percentage of cable weight to total weight	Difference in weight between			
					E_0 and 12 volts		E_0 and 24 volts	
	Total weight	Weight of cable	Weight of conduit		eq 14	eq 13	eq 14	eq 13
1	2	3	4	5	[b] 6	[b] 7	[b] 8	[b] 9
	lb	*lb*	*lb*	*Percent*	*lb*	*lb*	*lb*	*lb*
A	22.9	11.6	11.3	50.7	8	5	1	1
B	33.21	16.81	16.4	50.6	15	11	0	0
C	54.49	30.46	24.03	55.9	31	25	0	0
D	111.85	77.75	34.1	69.5	79	71.5	5.5	6.5
E	204.5	119	85.5	58.2	162	145	19	23

[a] Airplane *A* is a single-seat type; *B*, a two-seat type; *C*, a three-seat type; *D*, a small twin-engine type; and *E*, a large twin-engine type.

[b] Columns 6 and 7 show the difference between the weight of cable and conduit for the optimum voltage and that for 12 volts. Columns 8 and 9 show the difference between the weight of cable and conduit for the optimum voltage and that for 24 volts. Thus, if 24 volts is used instead of 12, airplane *C* will save 31 pounds according to columns 6 and 8, and 25 pounds according to columns 7 and 9.

V. CHANGES IN OPTIMUM VOLTAGES WITH K_2

The four curves in figure 5 show that as K_2 increases the optimum voltage decreases. The values are computed from eq 10, because this equation indicates greater changes in voltage with K_2 than eq 8 or 11. The values for the constants K_3' and K_4' were computed from the weights for a 12-volt system by taking 70 percent of the combined weight as the weight of the conductor and 30 percent of the total weight as the weight of the insulation and conduit.

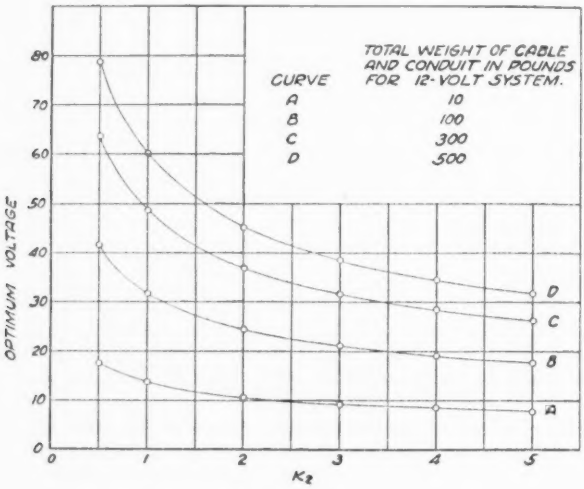

FIGURE 5.

Curves showing the change in optimum voltage with a change in K_2. Curves plotted from equation 10.

VI. DISCUSSION OF RESULTS

In determining the optimum voltage for a large number of airplanes, some of which are in use and some of which are not at this time designed, it was necessary to make broad but reasonable assumptions as to how the weight of electric equipment will change with voltage. The calculations for this change in weight are based upon the assumptions given in section II, as 1, 2, and 3, that all generators, batteries, cables, and conduits have a voltage-weight relationship which holds for all sizes of airplanes. The calculations may be said to apply to many classes of airplanes whose constants K_3', K_3'', and K_4' cover a range for which the ratio of the largest to the smallest value is 50:1.

The shape of the curves depends upon K_2, K_3, and K_4. The constant K_2 changes so slowly with a change in the size of the battery that it may be taken as a constant over a considerable range of battery sizes. K_3 and K_4 depend upon the weight of the cable and conduit, and by using these as parameters a family of curves is obtained all of which have the same general shape. The optimum voltages are determined by the shape of the curves rather than by their positions, and since the change in weight with voltage is slow in the neighborhood of the optimum voltage, the curves may be said

to have a minimum region. It is because of this slow rate of change in weight with voltage that such good agreement is obtained for the wide range of values when using the three diverse assumptions 3A1, 3A2, 3A3; 3B1, 3B2; and 3C1.

The assumption that the weight of the cable is 70 percent of the total weight of cable and conduit was true for only one airplane, as shown in column 5 of table 2. However, as shown in figure 3, the curves plotted from eq 14 for the smaller weight of cable and conduit are almost identical with the curves plotted from eq13, notwithstanding the difference in assumptions.

Curves 5 and $\overline{5}$ for all practical purposes are similar, although the weights are slightly different. For larger planes, such as indicated by the two curves 10 and $\overline{10}$, a separate auxiliary power unit will probably be necessary, and in this type of plane more than one voltage will be available. It will be noted that the shape of the two curves is nearly the same, and while there is a difference in weight, the selection of an optimum voltage from curve 5 will result in only a fraction of a pound change in weight over what would be the optimum weight on the basis of $\overline{5}$.

The curves are not plotted for eq 8, since using eq 8, is the same as taking a fractional part of the weight of wire and conduit and substituting these values in eq 10. Practically, this is the same as making the computations for a smaller airplane.

Referring to eq 11, it is seen that the optimum voltage depends upon the weight of cable and conduit and the constant K_2. This constant for the two larger batteries, for which curves are shown in figure 1, is for all practical purposes the same, since it changes less by doubling the capacity than the uncertainty of the other factors entering into this equation. This means that to a reasonable approximation the optimum voltage is independent of the watt-hour capacity of the battery, which seems somewhat paradoxical. In practice, this means that once the optimum voltage is determined, the discharge rate and output of the battery may be changed without affecting the optimum voltage, notwithstanding the total weight of the battery is changed by changing the output.

The increase in optimum voltage with a decrease in K_2 suggests that with more efficient battery construction a higher operating voltage is desirable. A recalculation of the values, using $K_2=0.85$ instead of 1, would indicate higher optimum voltages in columns 4, 5, and 6 of table 1.

The values given in table 2 are for $K_2=0.85$ and indicate that 24 volts is the optimum voltage for the single-engine type. For the twin-engine type, the voltage should be higher, but if a single voltage is to be selected for all classes of planes, 24 volts seems to place the additional weight only in the larger planes, which in most cases should be able to take care of this weight.

VII. CONCLUSIONS

Stated briefly, the equations indicate the following:

1. Although the computed weight of the system will change, the shape of the curves will be approximately the same whether the assumptions 1 and 2 are combined with 3A1, 3A2, 3A3; 3B1, 3B2; and

3C1, at least for the range of weights covered by table 1. The curves may be used to select the optimum voltage which will give approximately the minimum total weight in each case. The capacity of the battery selected will affect the absolute weight of this system, but the optimum voltage should not be greatly changed.

2. For airplanes of the single-engine type, standardization on 24 volts seems to meet the requirements for a large number of airplanes, and this voltage is in agreement with that used by several European countries. For airplanes having 10 pounds of cable and conduit or less, there may be an increase in weight of 5 pounds or more if one of the existing types of 24-volt batteries is used. If batteries having a smaller increase in weight with increasing number of cells are developed, the penalty for this choice of higher voltage will be less.

3. For large airplanes, where auxiliary power plants are used, it may be desirable to supplement the standard 24-volt generator-battery system with a higher voltage a-c or d-c system without battery.

The authors thank E. F. Mueller for his many helpful suggestions.

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SEPARATION AND COLORIMETRIC DETERMINATION OF RHENIUM AND MOLYBDENUM*

By James I. Hoffman and G. E. F. Lundell

ABSTRACT

The method herein presented for the separation and colorimetric determination of rhenium and molybdenum depends on differential reduction with mercury. If a dilute hydrochloric acid solution containing molybdate and perrhenate is shaken with mercury, potassium thiocyanate, and ethyl ether, only the molybdenum is reduced to the form which produces an ether-soluble colored compound with thiocyanate. The color of the ether extract serves for the determination of molybdenum. Addition of stannous chloride to the acid solution remaining after the molybdenum has been extracted produces a yellow to yellowish-red ether-soluble compound which serves for the determination of rhenium. As little as 0.001 mg of rhenium can be detected in a solution containing 10 mg of molybdenum, and 0.01 mg of molybdenum can be detected in the presence of 10 mg of rhenium. Few elements interfere in the determination of rhenium, and practically all of these can be eliminated by a simple distillation.

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I. GENERAL CONSIDERATIONS AND PRELIMINARY EXPERIMENTS

In a study of the volatilization of metallic compounds,[1] it became necessary to determine small amounts of rhenium in the presence of

*Originally presented by James I. Hoffman before the American Chemical Society, Boston Mass., September 15, 1939.

[1] James I. Hoffman and G. E. F. Lundell, *Volatilization of metallic compounds from solutions in perchloric or sulfuric acid*, J. Research NBS **22**, 469 (1939) RP1198.

molybdenum. Each element, if it occurs alone, can be determined by using the colored solution produced by the addition of thiocyanate and stannous chloride; but if the two occur in the same solution, the method fails.[2] Rhenium produces a solution which is more yellowish than the amber to cherry-red solution produced by molybdenum under the same conditions; however, experiments showed that the absorption of light by these solutions is so nearly in the same region of the spectrum that the two cannot be readily differentiated, even with the aid of filters.[3]

The method whereby molybdenum is converted to a xanthate complex and then extracted with chloroform [4] failed to give good results, because part of the molybdenum was converted to a blue compound which could not be extracted with chloroform.

If a solution containing molybdate and perrhenate in diluted hydrochloric acid (1+1)[5] is shaken with ethyl ether, most of the molybdenum passes into the ether and most of the rhenium remains in the acid. An extraction with ether, therefore, may be used to effect a partial separation; but for final determination a sharper separation is necessary. It should be noted that the thiocyanate which each element forms after controlled reduction is completely extracted by ethyl ether.

Differences in the stability of the thiocyanates toward the action of fluorides or hydrogen peroxide were noted, but these differences are not sufficient to permit the determination of one element without interference by the other. Molybdenum thiocyanate is bleached more rapidly by peroxides or by fluorides than is the corresponding compound of rhenium. The action of fluorides is so nearly selective that a considerable amount of experimental work was done before it was decided that this method would not be satisfactory.[6] Attempts of this kind were abandoned in favor of an investigation of selective reducing agents.

The molybdenum in the colored thiocyanate compound is variously stated to have a valence [7] of 3, 4, or 5, whereas rhenium in the colored compound which it forms with thiocyanate probably has a valence [8]

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[2] W. Geilmann, F. W. Wrigge, and F. Weibke, Z. anorg. allgem. Chem. **208**, 217 (1932).

[3] In preliminary experiments, spectrographs by C. J. Rodden, of the National Bureau of Standards, indicated that the molybdenum thiocyanate in ether solution showed general absorption at 400 to 520 mμ, and the corresponding rhenium compound at 400 to 500 mμ. No sharp absorption bands were noted in either case. For comparisons of solutions containing either element alone, it was therefore found convenient in much of this work to use a Wratten filter No. 45, with transmission from 430 to 540 mμ, in conjunction with a photoelectric comparator (or colorimeter). The Wratten filter No. 47A, with transmission between 380 and 520 mμ, would probably have been more satisfactory. The circuit was that of B. A. Brice, Rev. Sci. Inst. **8**, 279 (1937).

[4] This method was tentatively suggested by L. C. Hurd, Ind. Eng. Chem., Anal. Ed. **8**, 15 (1936).

[5] This denotes 1 volume of concentrated hydrochloric acid (sp gr 1.18) diluted with 1 volume of water. Diluted hydrochloric acid (3+200) denotes 3 volumes of the concentrated acid diluted with 200 volumes of water. If no dilution is specified, the concentrated reageant is meant.

[6] In a private communication, Loren C. Hurd stated that he independently came to the same conclusion concerning the action of fluorides.

[7] Latimer and Hildebrand, in Reference Book of Inorganic Chemistry, p. 289 (The Macmillan Co., New York, N. Y., 1933), give $MoO(CNS)_3$ as the formula of the colored compound of molybdenum. B. S. Hopkins, in Chemistry of the Rarer Elements, p. 260 (D. C. Heath & Co., New York, N. Y., 1923), gives $Mo(CNS)_4$ as its formula. Feigl, in Qualitative Analyse mit Hilfe von Tüpfelreaktionen, p. 175 (Akademische Verlagsgesellschaft, m. b. H., Leipzig, 1931), states that the molybdenum in the complex is trivalent and gives the formula $K_3Mo(CNS)_6$. It was found by us that the colored compound of molybdenum is formed if thiocyanate is added to solutions of quinquevalent molybdenum obtained by reduction either in the silver reductor by the method of N. Birnbaum and G. H. Walden (J. Am. Chem. Soc. **60**, 64 (1938)) or with hydriodic acid by the method of F. A. Gooch and C. Fairbanks (Am. J. Sci. (4), **6**, 168 (1898)). No color is produced if sexivalent molybdenum is treated with potassium thiocyanate alone, nor if it is reduced to the trivalent state in the Jones reductor, and the solution is allowed to flow into a solution of potassium thiocyanate, in the absence of oxygen. However, if the mixture is exposed to the air for some time, a slight color gradually appears, probably because of gradual oxidation of the molybdenum. These experiments indicate that molybdenum in the colored thiocyanate compound is quinquevalent. See also Studies of the Reducing Action of Mercury, by N. H. Furman and W. M. Murray, Jr., J. Am. Chem. Soc. **58**, 1689 (1936).

[8] Ind. Eng. Chem., Anal. Ed. **8**, 112 (1936).

of 6. L. C. Hurd and B. J. Babler give $ReO(CNS)_4$ as its formula. The object was to find a reagent that would reduce one of the two so that it would form the colored compound with thiocyanate, without affecting the other. Considerations of the electrode potentials, as well as actual trial, indicated that zinc, sulfur dioxide, chromous sulfate, titanous chloride, arsenious acid, and hydrazine were unsatisfactory. Rhenium is not reduced in the silver reductor under the conditions prescribed for molybdenum, but mercury seemed more convenient for effecting this differential reduction. It was finally found that if a dilute hydrochloric acid solution of molybdenum is shaken with mercury, the molybdenum is reduced to the valence required for the formation of the colored compound, but the rhenium is not affected. Moreover, it was found that, after extracting the molybdenum with ether, the rhenium can be determined with thiocyanate and stannous chloride in the usual way.

Rhenium is not reduced by mercury in 0.17 *N* hydrochloric acid (approximately 3+200); but then molybdenum, if present in large amount, tends to produce a blue compound which does not react with thiocyanate. In 2.2 *N* hydrochloric acid (approximately 1+4), the blue compound of molybdenum is not formed, but a trace of rhenium may be reduced and yield a color with thiocyanate. Two procedures are therefore given. In the one, the more dilute acid (3+200) is used for determining small amounts of molybdenum in the presence of relatively large amounts of rhenium; in the other, the more concentrated acid is used in the separation of small amounts of rhenium from large amounts of molybdenum. It was found that better extraction of molybdenum occurs in the presence of ferric iron. A little ferric chloride is therefore always added before reduction and extraction are started.

The essential steps of the method, together with modifications for different conditions, are given in the diagrammatic outline which follows.

II. PROCEDURE

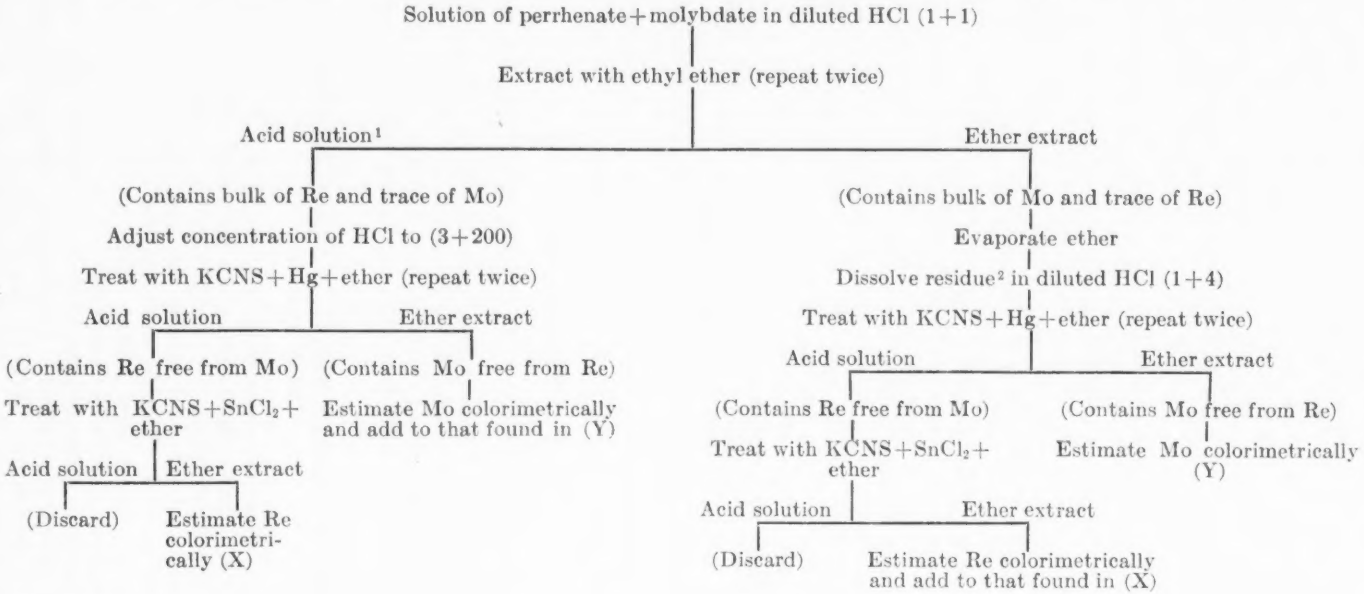
1. DIAGRAMMATIC OUTLINE OF PROCEDURE

In this outline, table 1, minor details, such as the additions of small quantities of iron and the washing of ether extracts with dilute acid, are omitted in the interest of clearness and brevity. For full details of the procedures, the reader is referred to the complete directions in the text.

2. PARTIAL SEPARATION OF RHENIUM AND MOLYBDENUM FROM EACH OTHER

To a solution of the two elements in 10 to 20 ml of diluted hydrochloric acid (1+1) add a slight excess of a saturated solution of potassium permanganate to make sure that the molybdenum and rhenium are present as molybdate and perrhenate, respectively. Add about 10 mg of iron as ferric chloride, and transfer the cool hydrochloric acid solution to a separatory funnel. Add 20 ml of ether, stopper tightly with a cork, and shake thoroughly for about 1 minute. Allow the ether and acid to separate into layers and drain the acid solution into another separatory funnel. Reserve the ether, which contains most of the molybdenum. Repeat the extraction with ether twice, adding 10 ml of ether to the acid solution each time. Reserve the

TABLE 1.—*Diagrammatic outline of the procedure for the separation and colorimetric determination of rhenium and molybdenum*


Solution of perrhenate+molybdate in diluted HCl (1+1)
Extract with ethyl ether (repeat twice)
Acid solution[1]
Ether extract
(Contains bulk of Re and trace of Mo)
Adjust concentration of HCl to (3+200)
Treat with KCNS+Hg+ether (repeat twice)
Acid solution
Ether extract
(Contains Re free from Mo)
(Contains Mo free from Re)
Treat with KCNS+SnCl2+ether
Estimate Mo colorimetrically and add to that found in (Y)
Acid solution
Ether extract
(Discard)
Estimate Re colorimetrically (X)
(Contains bulk of Mo and trace of Re)
Evaporate ether
Dissolve residue[2] in diluted HCl (1+4)
Treat with KCNS+Hg+ether (repeat twice)
Acid solution
Ether extract
(Contains Re free from Mo)
(Contains Mo free from Re)
Treat with KCNS+SnCl2+ether
Estimate Mo colorimetrically (Y)
Acid solution
Ether extract
(Discard)
Estimate Re colorimetrically and add to that found in (X)

[1]From this point the outline corresponds with section II, 4, p. 504, "Determination of small amounts of molybdenum in solutions containing relatively large amounts of rhenium."
[2]From this point the outline corresponds with section II, 3, p. 501, "Determination of small amounts of rhenium in solutions containing relatively large amounts of molybdenum."

acid solution. Combine the three ether extracts, add 10 ml of diluted hydrochloric acid (1+1), and shake vigorously for a few seconds. When the ether and acid have separated, draw off the acid and combine it with the reserved acid solution. Reserve the ether extract, which contains the bulk of the molybdenum and a trace of rhenium. Evaporate the combined acid solutions (which contain practically all the rhenium and a trace of molybdenum) nearly to dryness on the steambath and proceed as in II, 4, p. 504, "Determination of small amounts of molybdenum in solutions containing relatively large amounts of rhenium."

Cautiously evaporate the ether extract and proceed as in II, 3, p. 501, "Determination of small amounts of rhenium in solutions containing relatively large amounts of molybdenum."

The following examples indicate the separation that can be effected by this simple ether extraction of a solution containing the elements as perrhenate and molybdate, respectively. In a separation involving 2 mg each of rhenium and molybdenum, 0.12 mg of rhenium was found with the molybdenum in the ether extract and 0.09 mg of molybdenum remained with the rhenium in the acid extract. In a similar separation involving 10 mg of each element, 0.29 mg of rhenium was found with the molybdenum and 0.8 mg of molybdenum remained with the rhenium.

3. DETERMINATION OF SMALL AMOUNTS OF RHENIUM IN SOLUTIONS CONTAINING RELATIVELY LARGE AMOUNTS OF MOLYBDENUM

This procedure is applicable to solutions containing as much as 10 mg of molybdenum and not more than 1 mg of rhenium.

(a) SEPARATION OF THE TWO ELEMENTS

Add about 10 mg of iron as ferric chloride (if this amount of iron is not already present) and a drop or two of a saturated solution of potassium permanganate to the dry or nearly dry residue containing the rhenium and molybdenum. Then add a slight excess of ammonium hydroxide and heat for a few minutes on the steam bath to make certain that the elements are present as perrhenate and molybdate, respectively. Dissolve the residue in 25 ml of cool diluted hydrochloric acid (1+4) and add 2 ml of a 20-percent solution of potassium thiocyanate.[9] Transfer the solution to a separatory funnel containing about 25 g of mercury. Immediately add 20 ml of ether, stopper the funnel tightly with a cork, and shake vigorously until the acid solution above the mercury is colorless.[10] One minute of vigorous shaking usually suffices. As soon as the ether and acid have separated into layers, allow the mercury and acid to flow into another separatory funnel. Reserve the ether extract, which contains the bulk of the molybdenum.

To the separatory funnel containing the acid solution and the mercury, add 1 ml of a 20-percent solution of potassium thiocyanate and 15 ml of ether. Shake vigorously for 1 minute, allow the ether

[9] The residue sometimes dissolves with difficulty, but it goes into solution quite readily when the thiocyanate is added.

[10] If elements such as chromium, vanadium, cobalt, or nickel are present, the acid solution will have the color produced by these elements, but the shaking need be continued only until it is certain that the color of the ferric thiocyanate has disappeared.

to separate, and draw off the mercury and the acid layer as before. Reserve the ether extract.

Again add 1 ml of a 20-percent solution of potassium thiocyanate and 15 ml of ether to the funnel which contains the acid solution and the mercury. Shake vigorously, and allow the ether and acid to separate into layers.[11] Allow the mercury to run into a separatory funnel, and set it aside for use in future determinations. Next withdraw the acid layer which contains the rhenium [12] (solution *A*). Reserve the ether extract, and combine it with those previously obtained (solution *B*).

(b) DETERMINATION OF THE RHENIUM

To determine the rhenium, add 1 ml of a 20-percent solution of potassium thiocyanate and 1 ml of a solution of stannous chloride [13] to acid solution *A*, shake slightly, and allow to stand for 5 minutes. Add 20 ml of ether, shake vigorously, and allow the ether and acid to separate into layers. Allow the acid to drain into another separatory funnel, and twice repeat the extraction with ether, using 15 ml each time. Discard the acid solution. Combine the ether extracts, add 10 ml of diluted hydrochloric acid (1+4), shake vigorously, and then allow the ether and acid to separate into layers. Withdraw and discard the acid. This acid washing removes iron, which, if allowed to remain, gradually oxidizes and produces a pink color. Transfer the ether, which contains the rhenium, to a 50-ml flask, dilute to the mark with specially prepared ether,[14] and stopper tightly. Estimate the rhenium by comparing the color with that of a standard or set of standards prepared as follows: Transfer a suitable portion of a standard solution of rhenium [15] to a separatory funnel which contains 10 mg of iron as ferric chloride and 25 ml of diluted hydrochloric acid (1+4). Then add 2 ml of a 20-percent solution of potassium thiocyanate and 1 ml of stannous chloride solution. Shake slightly, allow to stand for 5 minutes, and proceed with the extraction of the rhenium and dilution of the combined ether extracts to exact volume, as was described for the solution under analysis. Typical results obtained in this determination are shown in table 2.

In the work involving less than 0.1 mg of rhenium, only one extraction with 20 ml of ether was made, and a series of standards was prepared which ranged from 0.01 to 0.10 mg at intervals of 0.01 mg. By using similar 30-ml test tubes and the same volume of ether (20 ml), the rhenium in the unknown could be estimated by direct observation, with the line of vision at right angles to the tubes. Differences of 0.01 mg can easily be distinguished in this way if there is less than 0.10 mg of rhenium in 20 ml of ether; but for concentrations greater

[11] If the ether layer at this point has no appreciable color, the extraction of molybdenum is complete. A distinct color in the ether indicates that another extraction should be made.

[12] From 1 to 5 percent of the rhenium passes into the ether during these extractions, but it is better to disregard this than to run the risk of extracting a trace of molybdenum and counting it as rhenium. Actually, the loss of rhenium here is without significance, because the total amount originally involved in this extraction seldom exceeds 0.5 mg. Tests have shown that the loss is proportional to the total amount of rhenium, and is not a fixed quantity.

[13] Dissolve 350 g of $SnCl_2.2H_2O$ in 200 ml of diluted hydrochloric acid (1+1). Dilute the *cool* solution to 1 liter with cold recently boiled water.

[14] To prepare ether for diluting stronger ethereal solutions of molybdenum or rhenium, transfer 25 ml of diluted hydrochloric acid (1+4), 2 ml of a 20-percent solution of potassium thiocyanate, and about 10 g of mercury to a large separatory funnel. Add 100 to 200 ml of ether, and shake vigorously for 1 minute. Allow the ether and acid to separate, and withdraw the mercury and acid. The ether is ready for use.

[15] Prepare a slightly acid solution containing 0.1 mg of rhenium in 1 ml. If a good grade of potassium perrhenate is available, this can be done by dissolving 0.155 g of the salt ($KReO_4$) in 1 liter of diluted sulfuric acid (1+99). For determining less than 0.1 mg of rhenium, it is convenient to dilute this solution to contain only 0.01 mg in 1 ml.

than 0.1 mg in 20 ml of ether, some form of colorimeter is necessary. If less than 0.01 mg is present, it is preferable to make the comparisons in Nessler tubes in the usual way, in a volume not exceeding 20 ml. Dilution of aliquot portions of more concentrated solutions of rhenium in ether yields fairly satisfactory standards for determination of small amounts of rhenium; but in this, as well as in the colorimetric determination of molybdenum, the best results are obtained if the quantity of standard is so chosen that but little dilution is necessary after the color has been developed.

TABLE 2.—*Results obtained in the determination of small amounts of rhenium in the presence of relatively large amounts of molybdenum*

Rhenium present	Rhenium found	Molybdenum present
mg	*mg*	*mg*
0.0010	0.0009	10
.0050	.0048	10
.0100	.0109	10
.080	.078	5
.100	.097	10
1.07	1.10	10

(c) DETERMINATION OF THE MOLYBDENUM

To determine the molybdenum, transfer the combined ether extracts (solution *B*, p. 502) to a separatory funnel, and add 10 ml of diluted hydrochloric acid (1+4). Shake vigorously; then allow the ether and acid to separate into layers. Withdraw and discard the acid. Then transfer the ether solution to a 100- or 200-ml volumetric flask, and dilute to the mark with specially treated ether. Mix thoroughly, and compare the color with that obtained by treating a standard solution of molybdenum [16] exactly as the solution under analysis was treated. The colorimetric comparison should be made without delay, because the color fades appreciably within two or three hours.

Because the standard solution may contain reduced molybdenum, the portion taken should always be heated with an excess of potassium permanganate before it is used. (See p. 499.) The addition of iron at the start must not be omitted, and the color must be developed by shaking with mercury as directed; otherwise, a slightly different color may be obtained.

In determining amounts of molybdenum between 1 mg and 10 mg, it has been found convenient first to develop the color in a 5-mg portion of the standard solution and then to dilute the combined ether extracts obtained from the standard to 100 ml in a volumetric flask. If the color of the solution under analysis appears to be lighter than the standard, dilution to 100 ml is satisfactory; but if it is darker, the solution in which the molybdenum is to be determined must be diluted to 200 ml, because a concentration of 0.05 mg of molybdenum in 1 ml is close to the upper limit at which satisfactory comparisons of color can be made.

[16] To prepare the standard solution of molybdenum, dissolve 1.5 g of pure sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, in 1,000 ml of water containing 5 ml of sulfuric acid. Standardize by reducing 50 ml of the solution in a Jones reductor and titrating with a standard solution of potassium permanganate. (See G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 319 and 325, J. Wiley & Sons, New York, N. Y., 1931 ed.).

4. DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM IN SOLUTIONS CONTAINING RELATIVELY LARGE AMOUNTS OF RHENIUM

This procedure is applicable to solutions containing as much as 10 mg of rhenium and not more than 1 mg of molybdenum.

(a) SEPARATION OF THE TWO ELEMENTS

Proceed exactly as in "Determination of small amounts of rhenium in solutions containing relatively large amounts of molybdenum" section II, 3, p. 501, but use diluted hydrochloric acid (3+200) instead of (1+4). The addition of iron and the treatment with permanganate at the start should not be omitted with the solution being analyzed nor in developing the color in the standard. Reserve the acid solution for the determination of the bulk of the rhenium (solution *C*).

(b) DETERMINATION OF THE MOLYBDENUM

Combine the ether extracts, which contain the molybdenum, and shake with 10 ml of diluted hydrochloric acid (1+4). Withdraw and discard the acid. Transfer the ether to a 50-ml Nessler tube or volumetric flask, dilute to exactly 50 ml with specially treated ether (see footnote 14), and stopper tightly with a cork. Without delay, compare the color with that obtained by treating a known amount of molybdenum exactly as the solution under analysis was treated.

The comparison of colors may be made with a colorimeter or in Nessler tubes. The best results are obtained if solutions containing nearly the same concentrations of molybdenum are compared. If a standard containing a small quantity of molybdenum (say 0.02 mg) is desired, it is better to develop the color in a solution containing this amount than to dilute a small aliquot portion of an ether extract having a high concentration of molybdenum. Typical results obtained in this determination are shown in table 3.

TABLE 3.—*Results obtained in the determination of small amounts of molybdenum in the presence of relatively large amounts of rhenium*

Molybdenum present	Molybdenum found	Rhenium present
mg	*mg*	*mg*
0.010	0.013	10
.020	.021	10
.040	.038	10
.100	.102	5
.200	.205	10
.400	.408	10
.500	.495	10
1.00	.97	10

(c) DETERMINATION OF THE RHENIUM

Transfer the acid solution (solution *C*) to a 200-ml volumetric flask, dilute to the mark with water, and mix thoroughly. Withdraw a 10-ml or a 20-ml portion, and add 5 ml of concentrated hydrochloric acid and about 10 mg of iron as ferric chloride. If necessary, adjust the volume to 25 ml by adding water. Then proceed with the addition of potassium thiocyanate and stannous chloride as described under "Determination of rhenium" (section II, 3 (b), p. 502).

By applying the entire procedure to a solution containing 10 mg each of rhenium and molybdenum, the amounts of the elements indicated in the various steps of the method, after the partial separation of perrhenate and molybdate with ether (section II, 2, p. 499), were as follows:

	mg
Molybdenum in ether extract by procedure II, 3 (c), p. 503	9.45
Molybdenum in acid solution by procedure II, 4, p. 504	.75
Total molybdenum	10.20
Rhenium in the ether extract by procedure II, 3 (b), p. 502	.29
Rhenium in the acid solution by procedure II, 4 (c), p. 504	9.68
Total rhenium	9.97

III. DISCUSSION OF THE METHOD

1. INTERFERING ELEMENTS

Unless otherwise stated, the tests for interferences by other elements were made by treating 2 mg of the element as if determinations of rhenium and molybdenum were being made.

Cerium, cobalt, chromium, gallium, germanium, indium, iridium, lead, nickel, osmium, ruthenium, thallium, and uranium showed no interference. By increasing the amount of chromium to 40 mg, a slight green tint was imparted to the ether, which interfered in the determination of both rhenium and molybdenum.

Platinum and rhodium interfere because they impart colors where rhenium or molybdenum should be indicated. Furthermore, they separate as the metals and thereby contaminate the mercury.

Vanadium interferes in the determination of molybdenum by imparting a color, but it does not interfere in the determination of rhenium. The interference is not serious. With 2 mg of vanadium, a color equivalent to only 0.01 mg of molybdenum was indicated.

Tungsten interferes by imparting a greenish-yellow tint to the ether where rhenium or molybdenum should appear.

Copper, gold, palladium, selenium, and tellurium do not impart colors to the ether, but they separate and contaminate the mercury. The presence of small amounts of these elements does not prevent the determination, but new mercury would probably be required for each analysis.

No tests were made with elements not mentioned above, but there is no reason to believe that any of them would produce colored solutions that would be extracted by ether.

2. APPLICATION OF THE PROCEDURES

Only in rare instances would it be necessary to use the whole procedure as given. The method was developed primarily to determine small amounts of the one element in the presence of relatively large amounts of the other. Usually, previous information concerning the material to be analyzed will permit the omission of the first part, II, 2, p. 499, "Partial Separation of Rhenium and Molybdenum from each other." More than likely only a trace of the one element in the presence of a relatively large amount of the other is to be determined. In such a case, the analyst can conveniently start with II, 3, p. 501, "Determination of small amounts of rhenium in solutions containing

relatively large amounts of molybdenum" or with II, 4, p. 504, "Determination of small amounts of molybdenum in solutions containing relatively large amounts of rhenium," whichever suits the particular material. If large amounts of both elements are present, other methods are more suitable than the colorimetric ones described herein, as for example, the methods using α-benzoinoxime [17] for molybdenum, or nitron [18] for rhenium.

The procedure is especially suitable for determining small amounts of rhenium in distillates obtained when solutions containing sulfuric or perchloric acid, together with hydrochloric or hydrobromic acid, are boiled. With the possible exception of chromium, such distillates contain no elements that interfere in the determination of rhenium; [19] but, in order to obtain a small volume and the proper concentration of acid, the rhenium in these distillates is best precipitated with hydrogen sulfide and then converted to perrhenate before the colorimetric determination is attempted. In testing such a procedure, small amounts of rhenium were transferred to a distilling flask containing hydrochloric and perchloric acids. The rhenium was then distilled by the procedure just mentioned. Small amounts of molybdenum were added to the distillate to simulate a solution which might be obtained by distilling rhenium from a material high in molybdenum. The solution, 100 ml in volume, was neutralized with ammonium hydroxide, 3 ml of sulfuric acid and 5 mg of trivalent arsenic (to act as a gatherer) were added, and the solution was saturated with hydrogen sulfide. After the solution had stood overnight, the sulfides were gathered on a small filter, and, without washing, were dissolved in ammonium hydroxide containing hydrogen peroxide. After evaporating the solution to dryness, the rhenium and molybdenum were determined by procedure II, 3, p. 501. Two trial analyses were made. In one, 0.010 mg of rhenium was added to the distilling flask and 0.020 mg of molybdenum to the distillate. The rhenium and molybdenum found were respectively 0.009 mg and 0.021 mg. In a similar analysis involving 0.005 mg of rhenium and 0.20 mg of molybdenum, 0.0045 mg of rhenium and 0.20 mg of molybdenum were found.

3. STABILITY OF THE COLORED COMPOUNDS OF RHENIUM AND MOLYBDENUM

Under the conditions outlined in the foregoing procedures, the color of molybdenum thiocyanate fades fairly rapidly. Comparisons should therefore be made as soon as possible (preferably within 1 hour) after the compound has been extracted. The color of the rhenium compound is rather stable. In observations made with the photoelectric colorimeter mentioned in footnote 3, p. 498, it was found that a standard containing 0.5 mg of rhenium in 50 ml of ether changed only about 3 percent in 4 days. The measurements at the single wave length of 435.8 mμ, described in the next section, showed that a solution 0.576×10^{-5} molar with respect to rhenium (1.0736 mg/liter) faded about 2.5 percent in 2 days, whereas one that was 2.9×10^{-5} molar (5.368

[17] H. B. Knowles, BS J. Research **9** 1 (1932) RP453.
[18] W. Geilmann und F. Weibke, Z. anorg. allgem. Chem. **195**, 289 (1931).
[19] See the tabulation on p. 467 of *Volatilization of Metallic Compounds from Solutions in Perchloric or Sulfuric Acid*, J. Research NBS **22** (1939) RP1198.

mg/liter) increased in color by 0.5 percent. It is obvious that such slight changes are not significant in the determination of small amounts of rhenium and that uncertainties caused by such changes in color disappear if the colors in the standards and the unknowns are developed at the same time. The fairly rapid fading of the color of the molybdenum compound obtained by reduction with mercury is a disadvantage and indicates that if molybdenum alone is to be determined, reduction with stannous chloride is preferable.

It should be observed that, throughout the procedure, final shaking of the ether extracts with dilute hydrochloric acid is recommended. If this is not done, gradual oxidation of the iron may cause a pink color which would result in positive errors.

4. SPECTRAL TRANSMITTANCY OF RHENIUM THIOCYANATE IN ETHER SOLUTION (BEER'S LAW)

Ether solutions of rhenium thiocyanate for measurements of spectral transmittancy were prepared by the procedure described for the preparation of the standards in "Determination of the rhenium" II, 3, b, p. 502. The measurements of transmittancy were made by H. J. Keegan, of the Colorimetry and Spectrophotometry Section of the National Bureau of Standards, with a General Electric recording spectrophotometer.[20] In each case the transmission of a 1-cm cell containing a given concentration of rhenium in ether solution was measured relative to that of a similar 1-cm cell filled with pure ethyl ether. The curves obtained with 2-day old solutions are shown in figure 1. The color in the very dilute solutions had a tendency to fade, and the more concentrated ones (as represented by curves 12 and 13) showed lower transmittancy with increased age. Although these curves are not quite consistent with those which would be obtained if Beer's law were obeyed, they do show the type of transmittancy curve and the wave length (432 mμ) of maximum absorption.

Additional measurements of transmittancy of freshly prepared solutions were made by K. S. Gibson with the König-Martens visual spectrophotometer [21] at the single wave length of mercury (435.8 m μ). These showed a slight deviation from Beer's law, but in the opposite direction from that indicated by the previous measurements. Apparently, the slight instability of the solutions makes it impossible to state with certainty, without extensive additional measurements, whether or not the solutions obey Beer's law.

5. CHOICE OF SOLVENTS FOR EXTRACTION

Throughout most of this work, ethyl ether was used for extracting the colored compounds of rhenium and molybdenum. Other solvents, for instance, amyl alcohol, ethyl acetate, or butyl acetate, can probably also be used. In a few determinations fairly satisfactory results were obtained with butyl acetate; but if the solvent must be evaporated, ether is preferable. In the partial separation of rhenium from

[20] See A. C. Hardy, J. Opt. Soc. Am. **25** (1935); J. L. Michaelson, J. Opt. Soc. Am. **28**, 365 (1938); K. S. Gibson and H. J. Keegan, J. Opt. Soc. Am. **28**, 372 (1938).
[21] H. J. McNicholas, BS J. Research **1**, 793 (1928) RP30.

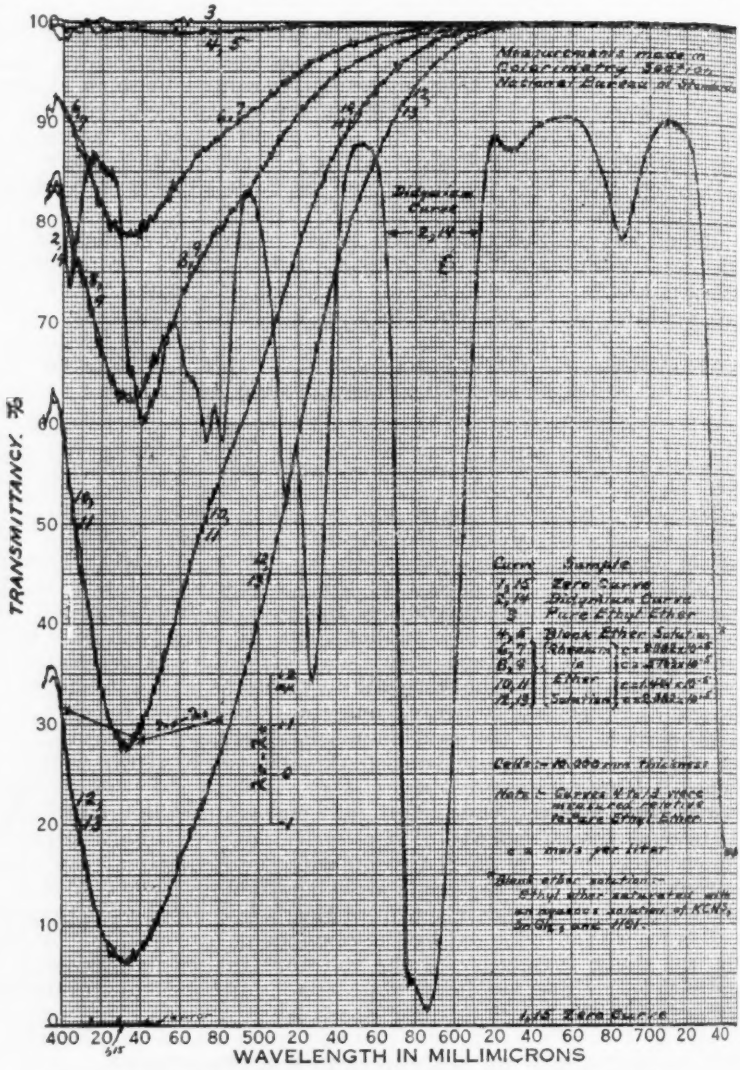

TRANSMITTANCY, %
WAVELENGTH IN MILLIMICRONS
Measurements made in Colorimetry Section, National Bureau of Standards
Dispersion Curve
Curve Sample
Zero Curve
Dispersion Curve
Pure Ethyl Ether
Block Ether Solution*
Ether Solutions
Cells = 10.000 mm thickness
Note: Curves 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 were measured against Pure Grade Ethyl Ether
c = mols per liter
*Block ether solution: Ethyl ether saturated with an aqueous solution of KCNS, 2c = 0.5 mols per liter.
1/15 Zero Curve

FIGURE 1.—*Transmittancy curves of rhenium thiocyanate solutions.*

molybdenum (section II, 2, p. 499), considerably better partition was effected by ether than by butyl acetate, and the ethereal solutions usually were clearer than those obtained with butyl acetate.

WASHINGTON, July 11, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1249

Part of Journal of Research of the National Bureau of Standards, Volume 23, October 1939

REFLUX REGULATOR AND HEAD FOR LABORATORY RECTIFYING COLUMNS[1]

By Frederick D. Rossini and Augustus R. Glasgow, Jr.[2]

ABSTRACT

A reflux regulator and head for laboratory rectifying columns is described that (a) has a nonlubricated glass valve, (b) utilizes a minimum of height above the rectifying section of the column, (c) provides for a substantially constant rate of removal of distillate for each setting of the valve, (d) provides for estimation of the "throughput" and the reflux ratio, (e) provides space for a thermometric device, and (f) has a flexible metal partition for permitting distillation at pressures below or above the prevailing atmospheric pressure.

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I. INTRODUCTION

A number of reflux regulators and heads for laboratory rectifying columns have been described in the literature, and their important features for various services have been discussed [1 to 15, 17 to 22].[3] Although each of the existing reflux regulators has advantages in some particular respects, none appears to fulfill all the special requirements arising in connection with the present work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards. These special requirements for the reflux regulator and head are that the device should (a) have a nonlubricated glass valve; (b) utilize a minimum of height above the column proper and permit the use of as long a rectifying section as possible; (c) provide for a substantially constant rate of removal of distillate from the column for a given setting of the valve (when the material being distilled is in one phase and is not too inhomogeneous with respect to density and viscosity); (d) provide for a rate of removal of distillate that is controllable within fairly small steps from zero to 100 percent of the material returning to the column from the condenser; (e) have, for distillation at pressures below or above the prevailing atmospheric pressure, a closed boundary between the distillation pressure and the atmospheric pressure that is made by a flexible partition rather than by a packing gland; (f) provide for convenient estimation of the rate of removal of distillate; (g) provide for convenient estimation of the throughput of

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[3] Figures in brackets indicate the literature references at the end of this paper.

the column; and (h) provide a suitable space for a small thermometric device (thermoelement or resistance thermometer).

This paper describes a reflux regulator and head that possesses the foregoing properties.

II. DESCRIPTION OF APPARATUS

Figure 1 gives an assembly drawing of the reflux regulator and head. *A* marks the connection to the rectifying section of the column. *B* is a U-tube, with drop counter on the return end, for returning the condensate to the rectifying section. *C* is a temporary funnel (later sealed off) for introducing additional packing into the rectifying section after the seal at *A* is made (if the rectifying section is a packed one). *D* is a condenser. *E* is a glass valve, consisting of a carefully ground plug and socket, which may be adjusted to remove any fraction of the overhead condensate. *F* is a metal-to-glass tapered joint. *G* is a metallic bellows (inside the metal housing). *H* is a knurled nut that moves the metal stem, *J*, longitudinally, without any rotary motion, to adjust the opening at the glass valve, *E*. *K* is a drop counter with connection to the receiver for the distillate. *L* is a connection to the atmosphere or controlled pressure or vacuum system. *M* is a tube for receiving a thermoelement or small resistance thermometer. *N* is a metal strap, covered on the inner side with asbestos paper, that is placed around the glass condenser and the metal tube, with the ends bolted together between the two, to provide additional support for the metal tube.

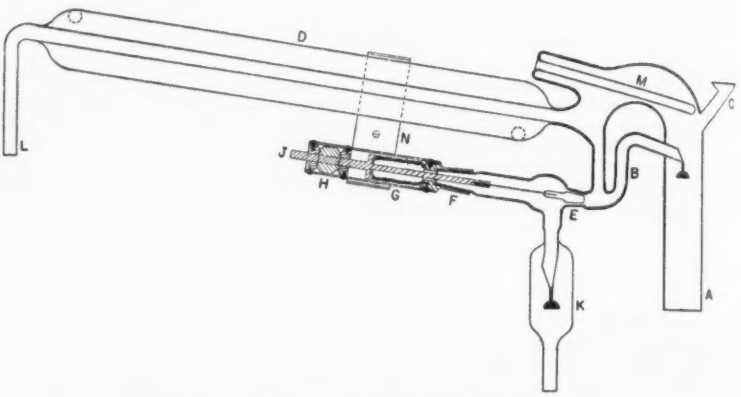

FIGURE 1.—*Assembly of reflux regulator and head.*

The metal-to-glass tapered joint is made with ordinary solder, according to the method described by Meyers [16], and provides a vacuum-tight and mechanically strong connection. It is necessary that a higher-melting solder be used in sealing the ends of the metallic bellows to the metal valve stem and the metal taper, in order that these two seals will remain vacuum-tight when the metal-to-glass connection at *F* is made with ordinary solder.

Figure 2 gives a detailed drawing of the glass part of the apparatus, and figure 3 that of the metal housing and control for the glass valve. These drawings are self-explanatory.[4]

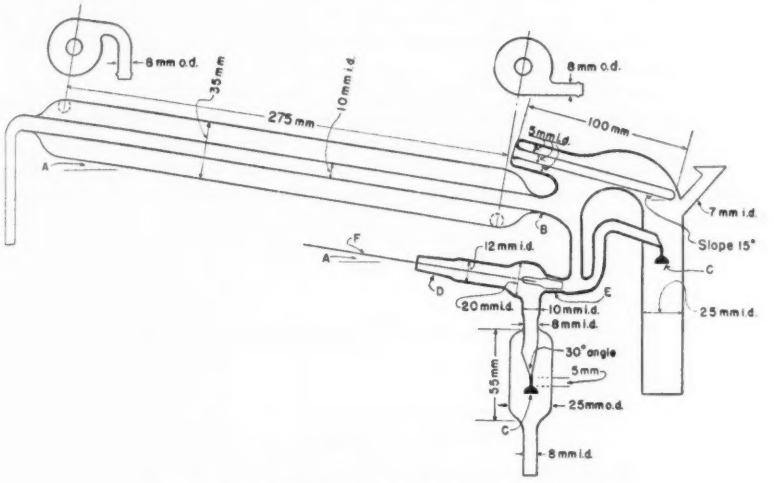

FIGURE 2.—*Details of the glass part of the apparatus.*

The letters have the following significance: *A*, slope 8½°; *B*, gradual slope, no pocket; *C*, drop counter, made hemispherical, ground flat on bottom, 8 mm in diameter; *D*, standard taper, male, No. 12/20, male, large end 12 mm, small end 10 mm, length 20 mm, ground for high vacuum, to fit metal female taper shown in Figure 3; *E*, taper, No. 6/10, male and female, large end 6 mm, small end 4 mm, length 10 mm, ground for high vacuum; *F*, tungsten wire, No. 18 AWG, hard soldered to the brass stem on one end and sealed into the ground-glass stopper on the other, length such that when the metal-to-glass joint (*F* in Figure 1) is made and the ground-glass stopper is closed in its seat, the sylphon bellows will be slightly compressed to make the distance *A* on the bellows in Figure 3 equal to 32 mm. The wall thickness of the glass should be extra heavy (1½ mm) where indicated by heavy lines, particularly at the base of the glass valve.

III. DISCUSSION OF APPARATUS

If the rectifying column is to be used entirely for distillation at atmospheric pressure, the metal housing and valve control shown in figures 1 and 3 may be replaced by the simpler one shown in figure 4, which is the same as the former with the exception that it is without the bellows. When the simpler metal control is used, it is desirable to increase the length of glass tubing between the valve at *E* and the taper at *F*, and possibly insert baffle plugs, in order to prevent significant loss of distillate by vaporization through the metal control.

If a mercury-in-glass thermometer is to be used, the thermometer tube, *M*, should be increased in length to provide the needed greater immersion. This can be accomplished by increasing the horizontal distance between the vertical rectifying section and the near end of the condenser.

[4] Because the dimensions of the bellows are more simply expressed in inches, the dimensions of the metal parts in figures 3 and 4 are all given in inches, except for the metal tapers, the dimensions of which are given in millimeters to conform with the units used for the glass apparatus.

To provide for the distillation of material whose vapors may react with the metal parts of the valve control, the exposed metal surfaces, especially the inner surface of the metallic bellows, can be covered with an inert flexible coating, such as Neoprene. The contact of the reactive vapors can also be reduced by lengthening the distance between the glass valve at *E* and the taper joint at *F* (fig. 1), and inserting one or more baffle plugs.

In actual operation, the U-tube, *B*, and the main tube, including the projecting part of the thermometer tube, are well-insulated thermally. The drop counters, which are made uniformly with 8-mm flat bottoms, deliver about 25 drops per ml of liquid for hydrocarbons of the gasoline range, and may be appropriately calibrated for various liquids.

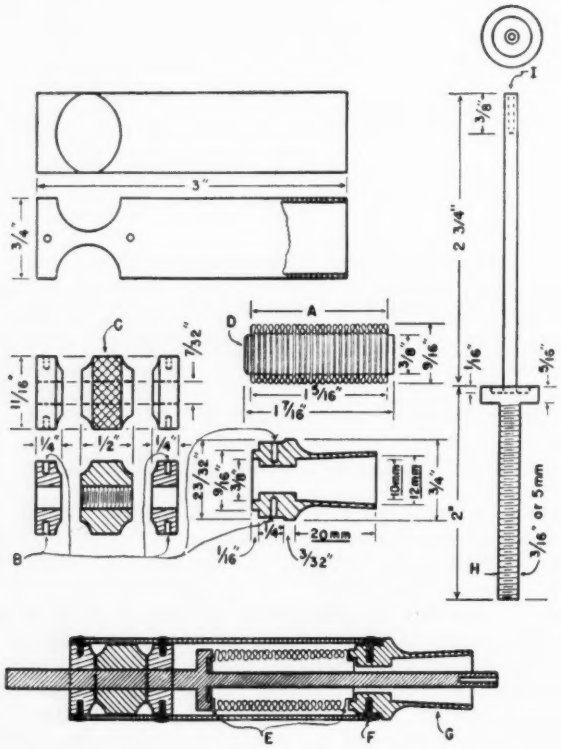

FIGURE 3.—*Details of the metal housing and control.*

The letters have the following significance: *A*, see *F* in legend of Figure 2; *B*, tapped for small screws, as 1.4 mm Loewenherz; *C*, surface of nut is knurled; *D*, sylphon bellows; *E*, ends of the sylphon bellows are hard-soldered to the two brass pieces, to hold high vacuum; *F*, brass tube is held in place by a close-fitting joint, fastened with screws as shown; *G*, standard taper, No. 12/20, female, large end 12 mm, small end 10 mm, length 20 mm; *H*, main shaft and knurled nut to be threaded about 50 threads per inch; *I*, hole 3/64 inch in diameter.

For a given setting of the glass valve, the constancy of flow of liquid through it is indicated by the following figures from observations taken at intervals of about ½ hr over an unselected 13-hr period, which gave the time in seconds for the fall of 10 drops: average of 27 observations, 61.8 sec; maximum deviation, 3.2 sec; average deviation, 1.1 sec.

In very little time, the valve can be set for any given rate of removal of distillate within about 10 percent, the smallest rate (other than zero) being of the order of 0.03 ml liquid per minute and the largest rate, with the valve wide open, being the entire overhead condensate.

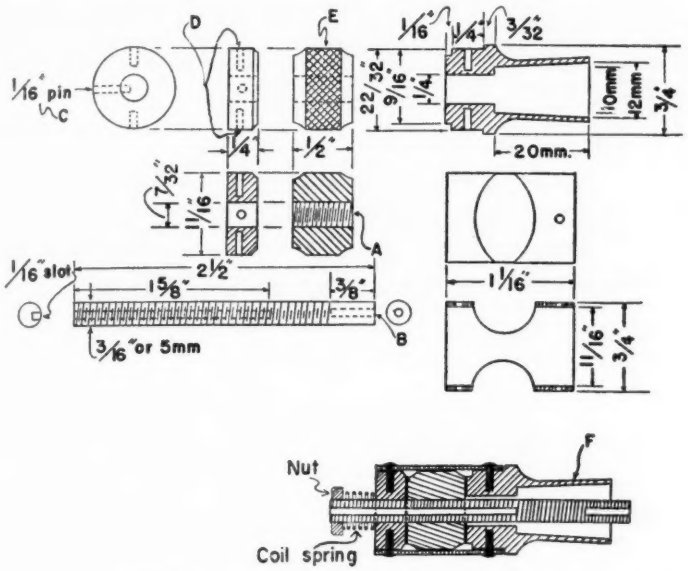

FIGURE 4.—*Simple metal control for glass valve.*

The letters have the following significance: *A*, nut threaded to fit the main shaft, about 50 threads per inch; *B*, hole 3/64 inch in diameter; *C*, slot to keep shaft from turning; *D*, holes tapped for small screws as shown; *E*, surface of nut is knurled; *F*, standard taper, female, No. 12/20, large end 12 mm, small end 10 mm, length 20 mm, wall thickness 0.8 mm.

In determining the throughput, rates below about 5 ml of liquid per minute may be estimated by means of the drop counter on the return end of the U-tube. Since this portion of the apparatus is thermally insulated, provision must be made for two removable plugs in the insulation layer, one in front of and one behind the drop counter, to permit observation of the falling drops. For larger rates the throughput may be estimated by opening the glass valve until no liquid returns to the rectifying section and measuring the volume of liquid collected (below *K*) in a given time, say 30 sec or 1 min. Larger rates may also be estimated by means of the drop counter inside the column by having that counter made with a bottom larger than 8 mm in diameter.

Acknowledgment is made of helpful suggestions received from E. O. Sperling, glassblower, and G. A. E. Rheinbold, mechanic, of the Division of Shops of this Bureau.

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WASHINGTON, August 4, 1939.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1250

Part of Journal of Research of the National Bureau of Standards, Volume 23, October 1939

SOIL-CORROSION STUDIES, 1937. CORROSION-RESISTANT MATERIALS AND SPECIAL TESTS

Kirk H. Logan

ABSTRACT

The soil-corrosion investigation begun in 1922 showed that many soils cause rapid corrosion of the commonly used pipe materials. The manufacturers of pipe have tried to develop materials more resistant to corrosion.

In 1932 some of these materials were buried in 15 corrosive soils for the purpose of determining their resistance to soil corrosion. Specimens are being removed at intervals of 2 or more years. The second group of specimens, including 41 metals and alloys and 11 protective coatings, was removed in 1937, and the results of their examination are contained in this paper. The results of several special tests are also given.

Several of the materials resisted very well most of the soils to which they were exposed, but none of them was unattacked by all of the soils.

The results indicate that pipe materials should be chosen with respect to the soils to which they are to be exposed.

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I. NATURE OF THE INVESTIGATION

The investigation of soil corrosion undertaken by the National Bureau of Standards in 1922 was intended primarily to determine the extent to which the corrosion observed in a study of electrolysis might be attributed to the corrosivity of the soil rather than to stray electric currents. For this purpose, specimens of the commonly used pipe materials were buried in typical soils of unknown corrosiveness

throughout the United States. This investigation resulted in the conclusions that (1) soils differed widely in corrosivity; (2) although most soils were not severely corrosive, very corrosive soils occurred in most parts of the country; and (3) the corrosion of the commonly used pipe materials depended more upon the type of soil to which the pipe was exposed than on the composition of the pipe. These conclusions, and the requests of users of pipe, resulted in many attempts to devise ways for reducing losses caused by the action of soils on pipes. These efforts took three forms, (1) development of materials expected to be more resistant to corrosion, (2) the production of new protective coatings, and (3) treatment of the soil or the metal to overcome the corrosive action of the soil.

To assist manufacturers in the development of corrosion-resistant materials, the National Bureau of Standards arranged with 15 public utilities and other operators of pipe lines for test sites and labor by means of which typical materials could be exposed to a variety of corrosive soils. In 1932 manufacturers were invited to submit specimens of materials for exposure in these sites. Because extensive studies of bituminous protective coatings had already been made, it was decided that such coatings should not be tested, but that new types of coatings would be accepted. The announcement of the proposed tests resulted in the burial in 1932 of 29 ferrous materials, 12 nonferrous materials, and 11 protective coatings. In 1934 some of these specimens were uncovered and removed [1, 2, 3].[1] The present paper is a report on the specimens that were uncovered and removed in 1937. The appearance of a set of these specimens after 5 years of burial in cinders is shown in figure 1. It should be noted that the corrosion of most of these specimens is more severe under this condition of burial in cinders than at any of the other test sites.

As an investigation reported in an earlier paper [4] showed that the maximum depth of pit observed depended in some degree upon the size of the area examined, an effort has been made in all the later investigations to have approximately the same area for all specimens. The usual 1932 specimen was a piece of 1½-inch pipe, 12 inches long, closed at both ends. However, it was not practical to adhere strictly to these dimensions for specimens of all materials. Some large- and some small-diameter pipes and some sheets were buried, the exposed areas being in most cases approximately the same as the external areas of the 1½-inch pipes, 12 inches long. (See fig. 1.)

The specimens were buried crosswise in the trench, at depths of 2 to 4 feet, the sheets being set on edge, so that both sides were exposed to the same conditions. It was found, however, when specimens were removed in 1934, that the top and bottom edges and the two sides of many of the sheet specimens had not corroded uniformly, as was expected, possibly because the specimen sheets had become displaced in position when the trenches were filled.

Experience has shown that there is at least one serious objection to such tests as have just been described. Although they permit a comparison of commercial materials, in most cases it is impossible to determine from an analysis of the data why one material or one soil condition is better or worse than another. This is because the

[1] Numbers in brackets indicate the literature references at the end of this paper.

FIGURE 1.—*Five-year-old specimens removed from cinders.*

UNIV. OF MICH.

materials and the soils differ in more than one respect. The data are therefore not entirely satisfactory for the development of other corrosion-resistant materials and for the determination of the causes of underground corrosion.

On the other hand, the justification for the tests as they have been conducted lies in the fact that in order to secure data suitable for the above purposes, it would be necessary to use alloys which were not commercial and to place them under soil conditions which are rarely if ever encountered by pipe lines.

Since the design of pipe materials and of pipe lines cannot be undertaken solely for the purpose of securing the minimum of corrosion, some of the scientific aspects of corrosion research have been sacrificed for the sake of obtaining data which will indicate the performance of available materials under service conditions.

II. CHARACTERISTICS OF THE TEST SITES

One of the most important results of the soil-corrosion investigation begun in 1922 was the evidence of the importance of soil characteristics in underground corrosion [4]. The results of the tests given in this paper can be understood only when considered in the light of the characteristics of the soils to which the materials were exposed.

It is possible that the performance of the materials was affected by the character of the backfill and by the weather conditions immediately prior and subsequent to the burial of the specimens. However, the characteristics of the soil determine to a large extent the effects of the backfill and of the weather on corrosion.

The soils with which this report deals were selected for the purpose of studying the resistance of pipe materials to underground corrosion. The governing principle in their selection, therefore, was that they should represent different kinds of corrosive conditions. Descriptions of these soils will be given in a later report.

The physical and chemical properties of the soils which might be expected to influence their corrosiveness are shown in table 1.[2] The aeration of the soils was estimated from careful inspection of the test sites, employing such criteria as the texture of the soil, degree of mottling, average depth of the water table, the depth at which mottling appears, and the depth at which the specimens were placed. The terms characterizing the degree of aeration are likewise indicative of drainage conditions except for those soils which, although naturally poorly drained, receive little or no rainfall.

The aeration or drainage of the soils is indicated by the value of the "air pore space," which is the percentage of the total volume of the soil occupied by air under specified conditions. This value is determined in the laboratory from the total volume of previously saturated soil which has been compacted centrifugally by a force of 1,000 times gravity, the volume of the water retained under this force, and the volume of the soil particles. These values naturally are not indicative of the aeration of those soils in which the natural drainage is restricted by the presence of an impermeable layer below the depth at which the specimens were buried.

[1] Prepared and discussed by I. A. Denison.

TABLE 1.—*Physical and chemical properties* [a] *of soils at test sites*

No.	Soil Type	Location	Mean temperature [b]	Annual precipitation [b]	Aeration [c]	Moisture equivalent	Air pore space	Apparent specific gravity	Volume shrinkage	Resistivity at 60° F (15.6° C)	pH	Total acidity mg-eq per 100 grams of soil	Composition of water extract—milligram equivalent per 100 grams of soil						
													Na +K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
			°F	*Inches*		*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Ohm-cm*									
51	Acadia clay	Spindletop, Tex	69	49	*P*	47.1	1.4	2.07	37.9	190	6.2	13.2	10.27	15.55	5.03	0.00	0.56	5.75	22.00
52	Alkali knoll	League City, Tex	69	47	*P*	54.8	3.7	[d] 1.97	33.9	234	8.8	[e] *A*	4.20	0.33	0.18	.52	1.36	1.33	1.26
53	Cecil clay loam	Atlanta, Ga	61.2	48.3	*G*	33.7	18.2	1.60	7.0	17,794	4.6	9.6							
54	Fairmount loam	Cincinnati, Ohio	53.2	38.6	*P*	26.1	4.7	1.96	6.1	886	7.0	3.5	0.59	10.10	.59	.00	0.70	0.08	9.05
55	Hagerstown loam	Baltimore, Md	55.4	42.6	*G*	32.0	15.5	1.49	8.6	5,213	5.8	10.9							
56	Lake Charles clay	El Vista, Tex	69	49	*P*	28.7	5.0	2.03	30.1	406	7.1	4.5	3.12	0.69	.47	.00	.80	1.59	3.04
57	Merced clay adobe	Tranquillity, Calif	63	8	*P*	40.9	5.1	1.89	29.5	128	7.7	*A*	23.40	13.50	4.51	.00	.34	1.15	37.50
58	Muck	New Orleans, La	69.3	57.4	*VP*	57.8	22.4	1.43	36.9	712	4.0	79.3	2.03	2.23	1.29	.00	.00	0.47	2.54
59	Peat	Kalamazoo, Mich	49	31	*VP*	43.6				1,659	5.5	33.3	1.03	3.08	2.70	.00	.00	3.47	1.04
60	do	Plymouth, Ohio	49	37	*VP*	43.4	33.2	1.28	9.1	218	2.6	297.4	2.91	10.95	2.86	.00	.00	0.00	56.70
61	Sharkey clay	New Orleans, La	69.3	57.4	*P*	30.8	2.3	1.78	16.4	943	5.9	8.6	0.73	0.68	0.33	.00	.71	.10	0.91
62	Susquehanna clay	Meridian, Miss	64.0	53.0	*F*	34.6	14.9	1.79	4.7	6,922	4.1	24.2							
63	Tidal marsh	Charleston, S. C	66.0	45.2	*VP*	46.7	19.5	1.47	18.8	84	2.9	100.2	33.60	6.85	4.00	.00	.00	12.70	36.60
64	Docas clay	Cholame Flats, Calif	58	16	*VP*	41.1	4.7	1.88	27.7	62	8.3	*A*	28.10	2.29	0.76	.00	.89	28.80	0.26
65	Alkali soil	Wilmington, Calif	62.4	15.2	*F*	26.4	15.8	1.41	5.7	148	7.2	*A*	7.65	12.40	2.20	.00	1.30	6.05	16.90
66	Mohave sandy loam	Phoenix, Ariz	69.7	7.8	*G*	16.5	20.1	1.79	2.7	232	8.7	*A*	6.55	0.51	0.18	.00	0.73	2.77	2.97
67	Cinders	Milwaukee, Wis	46.1	30.1	*VP*	11.1				455	8.0	*A*	0.77	3.03	.53	.00	.55	0.08	2.89
68	Gila clay	Phoenix, Ariz	69.7	7.8															
101	Billings silt loam	Grand Junction, Colo	52.0	8.8	*F*	30.0				261	7.3	*A*	5.21	19.24	1.43	.00	.66	1.56	22.48
102	do	do	52.0	8.8	*F*	20.4				103	7.3	*A*	22.63	16.56	3.85	.00	.56	4.67	36.82
103	do	do	52.0	8.8	*F*	30.6				81	7.3	*A*	22.01	13.32	2.00	.00	.18	11.09	25.70
109	Fresno fine sandy loam	Kerman, Calif	63	9	*P*	18.6				497	8.4	*A*	2.62	0.07	0.10	.31	.59	1.56	0.48
110	do	do	63	9	*P*	18.4				531	10.2	*A*	3.53	.07	.12	1.49	1.07	0.79	.25
111	do	Kernell, Calif	63	9	*P*	22.1				51	8.1	*A*	41.55	16.21	.44	0.00	.58	34.58	23.41
116	Merced clay	Los Banos, Calif	63.4	8.1	*F*	39.7				320	9.2	*A*	9.30	0.33	.18	4.60	2.10	1.17	1.57
117	Merced clay adobe	Tranquillity, Calif	63	8	*P*	51.8				106	8.5	*A*	36.19	14.66	.83	0.00	1.55	2.89	46.53
122	Panoche clay loam	Mendota, Calif	63	6.4	*F*	30.0				552	7.4	*A*	2.32	0.05	.26	.00	.70	0.07	1.40

[a] Determinations by I. A. Denison, R. B. Hobbs, and I. C. Frost.
[b] Data furnished by U. S. Weather Bureau. Values with no figures to the right of the decimal point are for some nearby city.
[c] Aeration of soils: *G*=good, *F*=fair, *P*=poor, *VP*=very poor.
[d] Measurement made on 20-mesh soil after centrifuging.
[e] *A*=alkaline.

The moisture equivalent was determined by the conventional method. The previously saturated soil was subjected to a centrifugal force of 1,000 times gravity for 40 minutes and the quantity of water retained by the soil was determined.

The apparent specific gravity of the soils in their natural state was determined by measurements made on undisturbed lumps of soil from the test sites. The lumps were immersed in a dish filled with mercury, and the volume of the lump was determined by measuring the volume of the mercury displaced. The weight per unit volume was then calculated by dividing the weight of the soil by its volume.

Shrinkage was determined by measuring the change in volume on drying of a previously saturated sample of soil which had been compacted by a centrifugal force of 1,000 times gravity. The shrinkage at 105° C was expressed as the percentage of the volume of the moist soil.

Resistivity of the saturated soils was determined with 60-cycle alternating current.

The water extracts used for chemical analyses were prepared as follows: A suspension of soil and water in the ratio of 1:5 was shaken mechanically at intervals for a total of 24 hours during a period of 72 hours. The extract was decanted into a 250-ml tall-form beaker and was filtered through a Berkfeld filter (12 by 2.5 cm) into a pressure flask by suction. As the difficultly soluble salts in the soil, such as calcium carbonate, which have an important influence on the rate of corrosion, reach equilibrium very slowly, a long period of extraction was adopted. It is possible, however, that reactions occurring during this prolonged extraction have reduced the quantity of the more soluble alkali carbonates in solution in the few soils in which these salts were present.

III. CHARACTERISTICS OF SOIL-CORROSION DATA

Because the specimens at different test sites have not been exposed for exactly the same periods, it has seemed advisable to reduce most of the corrosion data to rates of loss of weight and rates of maximum penetration. This procedure involves the assumptions that corrosion is a continuous process and that the results of the process are proportional to the duration of the exposure.

Neither of these assumptions is strictly true, and in some cases the errors are sufficient to be of importance. Underground corrosion is largely affected by the aeration and moisture contents of the soil and these factors are in turn affected by rainfall. The irregular way in which water is supplied to the soil and the fact that two localities may differ in the distribution as well as in the amount of rainfall are illustrated in figure 2, which shows the monthly average precipitation near four of the test sites from 1922 to 1936. The supply of water and oxygen to the specimens did not, of course, follow the rainfall exactly, since part of the water was lost through surface runoff, but it is obvious that the irregularities in the supply of water must produce effects on corrosion which are not measured by time. The curves show that the rainfall varies from month to month and from year to year and that these variations are not the same for different parts of the country. It must follow that corrosion progresses at an irregular

pace and that changes in the rates of corrosion at different test sites may not be synchronous.

It has been found also that at many test sites the average rate of corrosion tends to decrease as the test progresses. This decrease is much greater for some soils than for others. Rates of corrosion must therefore be used with great care in the comparison of soils or materials and in the estimation of losses or pit depths for periods greater than those for which test specimens were exposed.

As the progress of corrosion depends upon soil conditions as well as on time, it is not to be expected that when loss of weight or pit depth is plotted against the age of the specimens the result will be a smooth curve. The broken line resulting from such a procedure is the result of irregularities in weather conditions as well as of nonhomogeneous

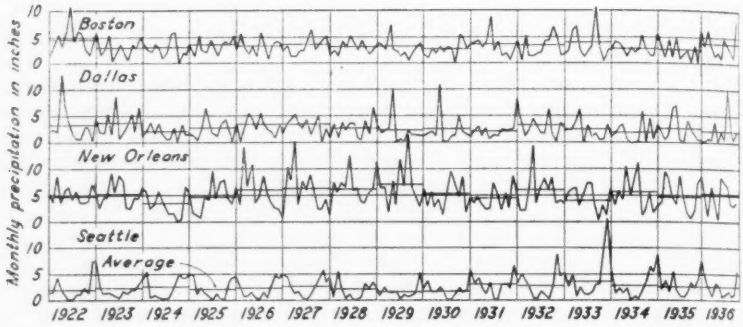

FIGURE 2.—*Average monthly precipitation near four test sites. (Data from record of U. S. Weather Bureau.)*

soil conditions, dissimilarity of specimens, and errors in observations. The mathematical relationship of time to maximum pit depths has been discussed in another paper [5].

In studying this report, the reader should keep the following facts in mind: (1) The rates of corrosion of ferrous and perhaps of other materials also, change with the period of exposure, especially when these periods are short. (2) The depth of the deepest pit on a large area will probably be greater than that on a smaller area exposed to nominally the same condition. (3) Because temperatures, soil moisture aeration, and other conditions do not remain constant throughout a field test or throughout the life of a pipe line, the results of field tests and of observations of corrosion on pipe lines are likely to be erratic. One or two observations may depart widely from the average of a larger number. The results of a sufficient number of tests show what may be expected on the average. The results of a few tests or observations show only what may happen, but give little information as to what should be expected in any single case representing nominally the same condition. For these reasons it is advisable to expose a large number of specimens whenever a test of soil corrosion is undertaken.

IV. FERROUS MATERIALS

The composition and dimensions of the ferrous materials removed in 1937 are given in table 2.

TABLE 2.—*Composition* [a] *and dimensions of ferrous materials*

Identification letter	Material	Nominal diameter or width	Length	Wall thickness	Carbon				Si	Mn	S	P	Cr	Ni	Cu
					Free	Combined	Total	For steel							
		Inches	*Inches*	*Inches*	%	%	%	%	%	%	%	%	%	%	%
A	Puddled wrought-iron pipe [b]	1.5	12	0.145				0.026	0.100	0.029	0.018	0.160			
B	do [c]	1.5	12	.145				.02	.125	.041	.018	.106			
C	Low-alloy cast-iron pipe	1.5	12	.25	3.0	0.5	3.5		2.5	.7	.05	.4	0.3	0.15	
D	Ni-Cu steel pipe	1.5	12	.145				.14	0.19	.21				2.47	1.08
E	High alloy cast-iron pipe	1.5	12	.145			2.98		2.13	1.0			2.61	15.0	6.58
F	Sand-coated cast-iron pipe	1.5	12	.250	2.9	.6	3.5		1.85	0.5	.75	.7			
G	Rattled cast-iron pipe	1.5	12	.250											
H	Cu-Mo open-hearth iron pipe [d]	1.5	12	.145			0.04		0.05	.32	.027	.016			0.52
I	Special cast-iron pipe	1.5	12	.350			2.53		1.43	.28	.077	.128			.51
J	do	1.5	12	.350			2.9		2.04	.83	.060	.248			.62
K	Cr-Ni steel sheet (18–8)	3	11	.025				.08	0.33	.44	.022	.015	17.2	8.95	
L	6-in. cast-iron pipe	6	5	.48	2.92	.83	3.75		1.49	.47	.08	.62			.07
M	3-in. cast-iron pipe	3	5	.39											
N	Low-carbon steel tube	2	10	.154				.15		.49	.030	.013			
P	Cr steel tube (5% Cr)	2	10	.154				.13		.46	.025	.012	5.05		
R	Cr-Ni steel tube (18–8)	1.5	12	.145				.05	0.28	.46	.011	.015	17.52	8.85	
S	Cr-Mn steel sheet (18–9)	6	10	.063				.07	.48	9.44			17.78		.74
T	Cr-Mn-Ni steel sheet	6	10	.063				.06	.40	6.09			17.76	3.83	.95
U	Cr steel sheet (12% Cr)	4	6	.063				.065	.28	0.38	.017	.011	11.95	0.482	.025
V	Cr steel sheet (17% Cr)	4	6	.063				.070	.34	.36	.015	.014	17.08	.092	.021
W	Cr-Ni steel sheet (18–8)	4	6	.063				.093	.42	.36	.017	.008	18.69	9.18	.016
X	Cr steel tube (18% Cr)	1.5	12	.145				.12	.277	.42	.017	.016	17.72	0.287	
Y	Cr-Ni steel sheet (22–12)	4	6	.063				.144	.59	1.80	.011	.015	22.68	12.94	.021

[a] These data were furnished by the manufacturers of the materials. In some cases, they may represent the average analyses of materials rather than of the specimens submitted for test.

[b] Oxide and slag, 2.560%.
[c] Oxide and slag, 2.681%.
[d] Molybdenum, 0.15%.

1. RATES OF LOSS OF WEIGHT OF THE SPECIMENS OF PIPE BURIED IN 1932

In tables 3 and 4 are given the rates of loss of weight of specimens of wrought-iron and steel pipe, and of cast-iron pipe, respectively, that were buried for 5 years. These rates are, in most cases, based on the examination of two specimens. Usually the two specimens of the same material in the same soil yielded results which agreed closely. Occasionally, however, they differed widely. In such cases the averages of the losses have little significance. For this reason those cases in which the loss of weight of the individual specimens differed from the average by 50 percent or more and was greater than 10 grams are indicated in the table by the superscript b. When the losses were small, relatively large differences between two specimens are unimportant, the significant fact being that the specimens corroded very little.

TABLE 3.—*Rates* [a] *of loss of weight of wrought-iron and steel pipe buried in 1932*

[Ounces per square foot per year [b]]

Soil		Duration of test	Puddled wrought iron	Puddled wrought iron	Cu-Mo open-hearth iron	Low-carbon steel	5% Cr steel	Cu-Ni steel	18% Cr steel	18% Cr, 8% Ni steel
No.	Type		*A*	*B*	*H*	*N*	*P*	*D*	*X*	*R*
		Years								
51	Acadia clay	5.45	2.31	2.49	2.13	2.34	2.67	1.52	.....	.....
53	Cecil clay loam	5.46	0.48	0.54	0.51	0.55	0.36	0.39	.....	.....
55	Hagerstown loam	5.20	.44	.46	.35	.42	.23	.26	.....	.....
56	Lake Charles clay	5.44	1.99	1.39	1.62	2.56	1.51	.94	.....	.....
57	Merced clay adobe	5.23	1.24	1.45	1.67	1.66	2.26	1.21	0.01	0.00
58	Muck	5.50	1.77	1.89	1.89	2.03	1.35	1.40	[c].15	.00
59	Peat	5.14	0.35	0.31	0.33	0.46	0.39	0.32	.....	.....
60	do	5.25	1.20	1.30	1.11	2.09	2.22	1.49	.....	.....
61	Sharkey clay	5.50	1.02	0.90	0.74	0.72	0.60	0.47	.....	.....
62	Susquehanna clay	5.47	0.74	.73	.75	.86	.48	.42	.0006	.00
63	Tidal marsh	5.55	.55	.44	.55	.82	.66	.41	.12	.02
64	Docas clay	5.22	4.23	4.42	4.49	4.85	4.62	4.51	[c].05	.002
65	Alkali soil	5.26	1.41	1.38	2.13	1.95	1.85	0.80	.....	.....
66	Mohave sandy loam	5.28	1.94	2.15	2.73	2.86	2.63	1.59	.....	.....
67	Cinders	5.26	6.04	4.73	4.76	6.59	[c]5.20	4.47	1.08	.00

[a] Average rates for 2 specimens, except for soil 57, from which 8 specimens were removed.
[b] Each ounce per square foot corresponds to an average loss of 0.0015 inch.
[c] Loss of weight of individual specimens differed from average by more than 50 percent.

It is impossible to make a strictly accurate comparison with respect to corrosion of the wrought and cast specimens because of the differences in the corrosion products. The boundary between corroded and uncorroded wrought iron or steel is well defined, and the corrosion products are easily removed. In cast iron the corrosion products are intermingled with uncorroded iron and graphite, and it was necessary to use a sharp-pointed tool with considerable force to remove the corrosion products.

The low losses of weight of the specimens high in chromium, *R* and *X*, in poorly aerated soils are surprising in view of the accepted theory which attributes the resistance of such materials to corrosion to a continual break-down and repair of an oxide film. The supply of oxygen in some of these soils was probably very limited, since they were wet and contained much organic matter.

TABLE 4.—*Rates* * *of loss of weight of cast-iron pipe buried in 1932*

[Ounces per square foot per year]

No	Soil Type	Cast iron *G*	Special-process cast iron *I*	Special-process cast iron *J*	Low-alloy cast iron *C*	High-alloy cast iron *E*
51	Acadia clay	3.38	4.55	4.20	5.37	0.76
53	Cecil clay loam	.37	.31	.34	.35	.14
55	Hagerstown loam	.45	.29	.28	.29	.12
56	Lake Charles clay	2.72	1.75	2.30	1.92	.85
57	Merced clay adobe	1.17	1.09	1.25	1.51	.32
58	Muck	2.19	2.26	2.08	2.60	.89
59	Peat	.50	.44	.48	.36	.07
60	do	1.36	1.38	1.37	1.27	.94
61	Sharkey clay	.88	1.02	1.13	.86	.32
62	Susquehanna clay	1.03	.77	.83	.84	.20
63	Tidal marsh	.58	.50	.65	.32	.10
64	Docas clay	4.17	5.10	5.12	5.97	.60
65	Alkali soil	1.17	1.54	1.75	2.32	.57
66	Mohave sandy loam	1.17	1.03	1.33	2.12	.57
67	Cinders	9.17	9.30	9.78	6.82	7.30

* Averages for 2 specimens except for soil 57, from which 8 specimens were removed.

Tables 3 and 4 also indicate that the ferrous pipes *D*, *E*, *R*, and *X* containing large percentages of alloying metals lost weight less rapidly than the other ferrous materials. No significant differences were observed in the weight losses in the low-alloy group.

The rates of loss of weight for most materials and most of the soils were less for the 5-year period of exposure than for the 2-year period, [1].

In Lake Charles clay all of the wrought materials except one variety of wrought iron and one containing 2.5 percent of nickel and 1 percent of copper showed higher rates of corrosion for the longer periods of exposure. None of the cast-iron pipes showed this unusual tendency and, until additional specimens, are examined, the significance of the apparent trend in the rate of corrosion of the wrought pipes must remain uncertain.

In the wet peat, soil 59, most of the specimens corroded at about one-fifth of the average rate of corrosion for the 15 soils, whereas the specimens in cinders corroded at approximately three times the average rate (fig. 1). Assuming that protection in soils should be proportional to their corrosiveness, it can be shown that protective measures based on the use of the average corrosiveness of the soils would result in the provision of five times as much protection as is required for the peat soil and only one-third of the protection needed in the cinders. This illustrates the hazard involved in the application of averages to specific soil conditions.

2. MAXIMUM PENETRATIONS OF THE FERROUS PIPES BURIED IN 1932

In tables 5 and 6 are given the averages of the depths of the deepest pits on the specimens of each variety of ferrous pipe buried in 1932. In those cases in which two varieties of pipe were quite similar in chemical composition and in their resistance to soil corrosion, the data for the two similar varieties have been combined. This permits the calculation of the standard errors for the averages of these specimens.

TABLE 5.—*Depths of maximum[a] pits on wrought ferrous specimens buried in 1932*

[In mils]

No.	Soil Type	Puddled wrought iron A	Puddled wrought iron B	Puddled wrought iron A+B Average	Puddled wrought iron A+B Standard deviation	Puddled wrought iron A+B Standard error	Cu-Mo open-hearth iron H	Steel Low-carbon N	Steel 5% Cr P	Steel N+P Average	Steel N+P Standard deviation	Steel N+P Standard error	Alloy steel 2.5% Cu, 1.1% Ni D	Alloy steel 18% Cr X	Alloy steel 18% Cr, 8% Ni R
51	Acadia clay	144	[b]129+				[c]145+	154+	105				55		
53	Cecil clay loam	64	71	67	5	3	65	50	56	53	5	3	26		
55	Hagerstown loam	79	84	81	3	2	75	57	65	61	9	5	34		
56	Lake Charles clay	66	65	66	9	5	65	71	154+	112+	44	25	42		
57	Merced clay adobe	94	100+	97	21	8	113+	100	84	92	22	8	71	[b]10	0
58	Muck	68	64	66	9	5	60	103	70	86	18	11	71	[b]66	0
59	Peat	25	18	21	3	2	5	20	32	26	7	4	3		
60	do	38	37	37	6	4	[b]21	24	67	45	22	13	26		
61	Sharkey clay	41	37	39	9	5	[b]59	[b]54	[b]37	45	28	16	30		
62	Susquehanna clay	54	56	55	7	4	86	66	83	75	13	8	46	4	0
63	Tidal marsh	22	37	30	9	5	[b]49	36	87	61	30	17	17	96	1
64	Docas clay	129	110	119	13	8	137	154+	154+	154+	0	0	108	10	1
65	Alkali soil	91	87	89	13	8	97	74	107	88	14	8	48		
66	Mohave sandy loam	85	106	95	23	13	145+	154+	133	144+	12	7	75		
67	Cinders	145+	145+				118+	119+	112+				145+	145+	0

[a] Average of the deepest pit on each of 2 specimens except for soil 57, from which 8 specimens were removed. All specimens were approximately 5 years old; see table 3 for exact ages.
[b] Pit depths on individual specimens differed from average by more than 50 percent.
[c] + indicates that one or more specimens were punctured.

TABLE 6.—*Depths of maximum pits[a] on cast-iron pipe buried in 1932*

[In mils]

No.	Soil Type	Horizontally cast in sand mold F	Horizontally cast in sand mold G	F+G Average	F+G Standard deviation	F+G Standard error	Special process I	Special process J	I+J Average	I+J Standard deviation	I+J Standard error	Low-alloy C	High-alloy E
[b]51	Acadia clay	[b]250+	250+	[c]			305+	309+	[c]			185+	50
53	Cecil clay loam	49	51	50	7	4	47	45	46	11	6	40	36
55	Hagerstown loam	66	50	58	14	8	56	59	57	9	5	58	37
56	Lake Charles clay	119	109	114	14	8	98	93	95	21	12	101	32
57	Merced clay adobe	76	81	78	15	9	65	76	70	11	6	90	[d]70
58	Muck	104	179+	142+	64	37	107	109	108	20	11	124	34
59	Peat	52	33	42	10	6	43	35	39	12	7	11	14
60	do	60	68	64	13	7	50	57	54	9	5	72	[d]80
61	Sharkey clay	48	55	51	18	11	83	60	72	13	7	44	39
62	Susquehanna clay	66	95	81	20	11	71	80	76	5	3	76	49
63	Tidal marsh	43	74	58	28	16	60	83	72	26	15	12	16
64	Docas clay	116	126	121	12	7	116	104	110	15	9	146	27
65	Alkali soil	74	94	84	23	14	95	100	97	4	2	91	42
66	Mohave sandy loam	71	79	75	10	6	60	70	65	9	5	120	36
[b]67	Cinders	250+	250+	[c]			[d]217+	[d]210+	[c]			185+	250+

[a] Average of deepest pit on each of 2 specimens except for soil 57, from which 8 specimens were removed. All specimens were approximately 5 years old.
[b] + indicates that one or more specimens were punctured.
[c] Soils 51 and 67 are not included in the average, because there are too many holes in the specimens.
[d] Pit depths on individual specimens differed from average by more than 50 percent.

The standard errors indicate the reproducibility of the averages and are useful in deciding whether the difference between two averages is characteristic of the materials or due to chance. The decision may be based upon the standard error of the difference between two averages. If the averages are derived from the same number of observations, this may be computed by the equation [6]

$$\sigma^2_D = \sigma_1^2 + \sigma_2^2,$$

in which σ_D is the standard error of the difference between the two averages, and σ_1 and σ_2 are the standard errors of the two averages. Tables showing the probability of an occurrence of a deviation greater than some multiple of the standard errors of averages will be found in many textbooks on statistics.

Open-hearth iron, *H* (table 5), differed from the puddled irons, *A* and *B*, in the process of manufacture and in that material *H* contained small amounts of copper and molybdenum, whereas the puddled iron contained slag inclusions. The deepest pit shown for material *H* is less than the average of the deepest pits on materials *A* and *B* in 7 of the 15 soils, but in most cases the differences in the pit depths are so small that they may be fortuitous.

Materials *N* and *P* differed only in that the latter contained about 5 percent of chromium. The material without chromium, *N*, developed shallower maximum pits than material *P* in 8 of 13 soils. Holes in both materials prevented a comparison in two soils. The averages of depths of the maximum pits of the puddled-iron specimens, *A* and *B*, are less than for the averages of the open-hearth steel specimens, *N* and *P*, in 9 of the 15 soils, but again the differences are not marked in most cases and may be due to chance. Although it seems logical that one material might be superior under some soil conditions and inferior under others, the writer has been unable to associate any soil characteristics with the apparent superiority of any of the materials so far discussed.

With respect to pit depths, nickel-copper steel, *D*, appears to be definitely superior to the other materials so far discussed, although in 13 of the 15 soils the maximum pits on material *D* were deeper than those on some of the other materials. In three cases the differences were not large.

The specimens of pipe, *R* and *X*, which contained about 18 percent of chromium, were placed in only six soils. In all soils the pitting of material *R*, which contained 18 percent of chromium and 8 percent of nickel, was definitely the least.

Table 6 shows the averages of the maximum pit depths for two specimens of six varieties of cast iron. Only material *E*, which contained about 15 percent of nickel and 6 percent of copper, was definitely superior to the others with respect to pit depths. This material was also superior, with respect to maximum pit depths, to the wrought materials in table 5, with the exception of materials *D*, *R*, and *X*, which contained chromium.

Materials *F* and *G* differed only in that the adherent molding sand was left on material *F*. This material may have been slightly superior to material *G*, but the difference was not great, perhaps because the surface of material *F* was not completely covered by sand. On the other hand, the spots where the casting risers were removed

were painted with portland cement, which slightly reduced the area of the pipe exposed to the soil. The cement may have slightly reduced the acidity of the soil adjacent to the spots.

The relative rates of corrosion of cast iron and steel have been of interest to many pipe users. A little light on this matter may be obtained by comparing the data for averages of materials *F* and *G*, table 6, with the averages of materials *N* and *P*, table 5. Such a comparison is shown in table 7, from which it can be seen that there were six soils in which real differences in the materials appeared. This table indicates that the cast iron pitted less than steel in the alkali soils and more deeply than steel in the acid soils.

TABLE 7.—*Comparison of specimens of 2-inch steel pipe and 1½-inch cast-iron pipe with respect to pitting in acid and alkali soils*

[Based on a comparison of the averages of the depths of the deepest pits on specimens *N* and *P* with the corresponding averages for specimens *F* and *G*]

Acid soils			Soils with acidity less than 14 mg-eq per 100 grams of soil			Alkali soils			Soils in which both materials were punctured
Soils in which the deepest pit was on cast iron	Soils in which the deepest pit was on steel	Soils in which the difference was less than 7 mils	Soils in which the deepest pit was on cast iron	Soils in which the deepest pit was on steel	Soils in which the difference was less than 7 mils	Soils in which the deepest pit was on cast iron	Soils in which the deepest pit was on steel	Soils in which the difference was less than 7 mils	
Identification No.		*Identification No.*			*Identification No.*		*Identification No.*	*Identification No.*	*Identification No.*
58	None	62	None	None	53	None	57	65	6
59	do	63	do	do	55	do	64		6
60	do		do	do	56	do	66		
					61	do			

It is doubtful, however, whether the relative pit depths on the two materials should be associated with soil acidity or alkali content, since, in the 12-year tests [1], some of the alkali soils were very corrosive with respect to cast iron, whereas the 10 soils in which the pit-cast iron specimens, *L*, were slightly superior to the open-hearth steel specimens, *K*, all contained some acid. Table 11, page 533, throws some additional light on this subject.

3. CHANGES IN RATES OF MAXIMUM PENETRATION

A comparison of the data on pit depths after 5 years, as given in tables 5 and 6, with similar data for 2-year-old specimens [1] shows that in general the rates of penetration based on exposures of approximately 5 years are much less than those for exposures of 2 years. However, all materials except *D* and *E* showed increased rates of penetration for the 5-year period in Lake Charles clay, and one or more materials showed increased rates of corrosion in one or more other soils. No material showed a decreased rate of penetration for the 5-year period of exposure in all soils. The increases were in most cases small and many of them at least may be attributed to chance. Nevertheless, such chance results are not altogether unimportant since the probability of an abnormally deep pit on a specimen must be much less than the probability of a similarly abnormal pit on a pipe having a much larger area. Indeed, the abnormal occurrences

constitute an important consideration in underground corrosion, since dependability is often a primary consideration in underground construction.

4. FERROUS PIPES IN MERCED CLAY ADOBE

Changes in the operations of one of the cooperators necessitated the removal of all the specimens from Merced clay adobe (site 57). This made available the data for eight specimens of each material for the computation of the averages of the losses of weight and of maximum pit depths. These calculations permit a fairly satisfactory comparison of the materials in this soil. For each material the aver-

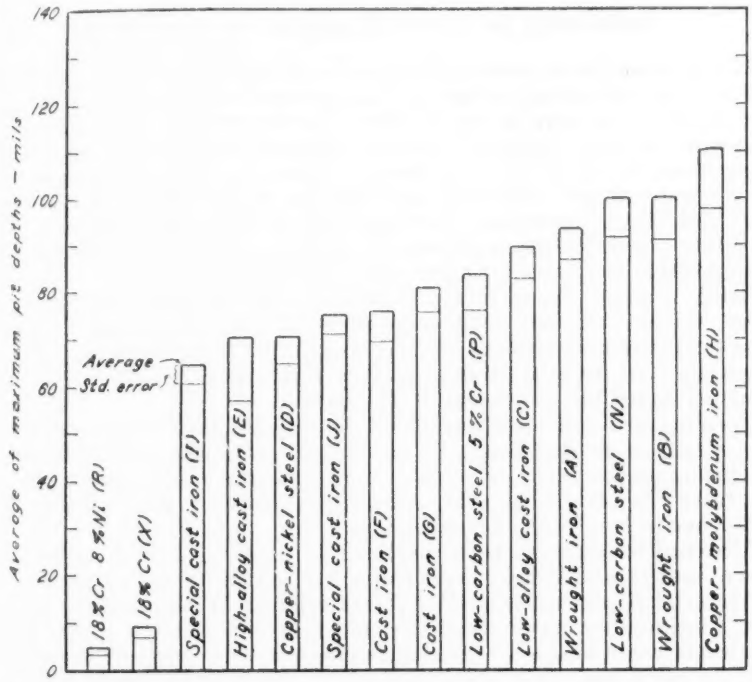

FIGURE 3.—*Averages of maximum pit depths on ferrous pipes removed from Merced clay adobe after an exposure of 5 years.*

age of the deepest pit on each specimen and the standard error of the average is shown graphically in figure 3.

Obviously, the average of the depths of the deepest pits on the materials containing 18 percent of chromium are much less than those for the other ferrous materials. The number of pits on the chromium alloys was also much smaller. The averages of the maximum pit depths for the other materials do not differ greatly, but the differences are sufficient in some cases to appear to be significant. This is especially true of differences between the maximum pit depths of

materials *I*, *J*, and *C*. Figure 3 suggests that the molding sand left on material *F* may have been somewhat beneficial, since the maximum pit depths on this material are somewhat less than on material *G*, from which all sand was removed. A large number of comparisons could be made and for each comparison the probability of there being a real difference can be determined by the equation previously given. The relative resistances to corrosion shown in figure 3 may not hold for other soil conditions. Thus the figure indicates that the maximum pit depth for material *P* is considerably less than for material *N* in Merced clay adobe, whereas table 5 indicates that in 8 of 15 soils the maximum pit depths are less for material *N* than for material *P*.

5. CORROSION OF CHROMIUM-IRON ALLOY SHEETS

Seven varieties of ferrous alloy sheets, all containing chromium and six of them containing nickel and manganese and one only chromium and manganese, were buried in 1932. Unfortunately, the decision to test most of these materials was not reached until it was too late to place them in all of the test sites. Moreover, because some of the alloys were rather expensive and because they were thought to be very resistant to corrosion, the sheets were of light-gage material. As a result, several of the specimens have been punctured, which makes it impossible to determine their rates of penetration.

Table 8 shows the results of the examination of specimens of Cr-Fe alloy sheets removed after exposures of approximately 5 years. The following comparisons are based on the assumptions that differences in heat treatment and surface finish and condition are not responsible for the differences in the data.

Specimens *U* and *V* differed chiefly in that the latter contains about 50 percent more chromium. The material with the greater amount of chromium lost definitely less weight in three of the seven soils of the test. In two of the other soils, the losses were so small that the difference in losses may be accidental.

Material *S* appeared to be superior to material *T* with respect to loss of weight and inferior with respect to maximum pit depths.[3]

Material *K* was quite similar to material *W* in composition, but it lost considerably more weight in most of the soils to which both materials were exposed. The differences in the areas of the specimens is insufficient to explain this. Material *K* had a bright polished surface which is generally supposed to be favorable to corrosion resistance. In soil 60, one side of one of these specimens was badly corroded, but the other side and both sides of the other specimen of this material were corroded very little. Material *Y* corroded more than material *W* in six of the seven soils to which both were exposed, although material *Y* contained more chromium, nickel, and manganese than material *W*. Both of these materials corroded only very slightly in any of the soils, although some of the soils were very poorly aerated.

A comparison of the 2- and 5-year data on the sheet specimens tends to indicate a decreased rate of loss for the older sheet specimens, but there are a number of exceptions to this conclusion.

[3] Table 19, page 464, of Research Paper RP883 [1] tends to confirm these observations, but the data are altogether too limited to justify a conclusion.

TABLE 8.—*Average loss of weight and maximum penetration of corrosion-resisting steel*

TABLE 8.—*Average loss of weight and maximum penetration of corrosion-resisting steel*

No.	Soil Type	Duration of test	(5)[a] 11.95% Cr, 0.48% Ni, 0.38% Mn			(5) 17.08% Cr, 0.09% Ni, 0.36% Mn			(2) 17.72% Cr, 9.44% Mn			(1) 17.76% Cr, 3.83% Ni, 6.09% Mn			(2) 17.2% Cr, 8.95% Ni, 0.44% Mn			(5) 18.69% Cr, 9.18% Ni, 0.36% Mn			(5) 22.68% Cr, 12.94% Ni, 1.80% Mn		
			Loss			Loss			Loss			Loss			Loss			Loss			Loss		
			Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration	Average	Standard error	Maximum penetration
			U			*V*			*S*			*T*			*K*			*W*			*Y*		
		Years	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*	*Grams*	*Grams*	*Mils*
51	Acadia clay	5.45													0.38		[b]25+						
53	Cecil clay loam	5.46													.009		0						
55	Hagerstown loam	5.20	0.006	0.0008	1	0.0026	0.0033	0										0.0052	0.0024	3	0.023	0.020	1
56	Lake Charles clay	5.44													.37		25+						
57	Merced clay adobe	5.23	2.2	1.5	63+	.90	.71	34+	0.12	0.10	9	0.50	0.57	5	.015	0.009	1	.006	.0021	3	.014	.008	3
58	Muck	5.50													.021		0						
59	Peat	5.14	.004	.0017	3	.008	.002	1							.018		2	.007	.001	0	.020	.0058	3
60	do	5.25	[c]47	58	[c]27+	6.9	14	[c]15							[c]10		[c]14+	.005	.0017	4	.009	.0014	3
61	Sharkey clay	5.50													.021		0						
62	Susquehanna clay	5.47													.019		0						
63	Tidal marsh	5.55													.048		2						
64	Docas clay	5.22	9.4	1.4	63+	2.6	.88	54+	4.3		63+	7.5		5	.031		3	.017	.0028	4	.016	.0081	3
65	Alkali soil	5.26	.95	0.75	43	1.4	.76	36+							.019		0	.0036	.0012	3	.012	.0057	3
66	Mohave sandy loam	5.28	2.9	.63	54+	3.1	1.7	11+							.93		[c]14+	.006	.0022	2	.014	.0061	3
67	Cinders	5.26							.013		8				.015		0						

[a] The number in parentheses indicates the number of specimens removed from each test site except for soil 67, from which 4 times this number of specimens have been removed.

[b] +indicates that 1 or more specimens contained holes because of corrosion, rendering the computation of the exact penetration impossible. The thickness of the specimen has been used as the maximum pit in this case.

[c] Loss or maximum pit for 1 or more specimens was greater than the average by more than 50 percent.

6. CORROSION OF BOLTS

Specimens of four kinds of malleable iron and steel bolts were removed from three soils after exposures of approximately 5 years. The bolts were of ¾-inch stock and were approximately 4 inches long. Table 9 shows the losses of weight and depths of the deepest pits on the heads of the specimens.

TABLE 9.—*Corrosion of ¾-inch bolts* [a]

Soil				Malleable iron						Steel	
No.	Type	Number of specimens of each kind	Duration of test	Loss (average)	Average of maximum pit on heads	Loss (average)	Average of maximum pit on heads	Loss (average)	Average of maximum pit on heads	Loss (average)	Average of maximum pit on heads
				Decarburized *A*		Not decarburized *B*		High strength *C*		*D*	
			Years	*Grams*	*Mils*	*Grams*	*Mils*	*Grams*	*Mils*	*Grams*	*Mils*
57	Merced clay adobe	4	5.23	11	61	13	79	12	44	10	35
59	Peat	2	5.14	5.6	3	4.6	3	5.3	3	6.1	12
61	Sharkey clay	2	5.50	8.7	18	11	35	9.6	27	10	43

[a] These bolts were 4 inches long.

The measurement of pits was confined to the heads of the bolts, because accurate pit measurements on the bodies of the bolts were impracticable. Figure 4 shows the deepest pit on the body of each specimen. Because of the very limited amount of data and the wide dispersion of the measurements, it is impossible to reach a definite conclusion as to the relative merits of the materials. It does not appear, however, that the corrosion of the materials tested is materially affected by any differences they may possess.

7. COMPARISON OF MAXIMUM PIT DEPTHS ON SPECIMENS OF DIFFERENT DIAMETERS

Table 10 affords an opportunity to compare the depths of the maximum pits on materials of different dimensions on three different bases. From each soil there were removed one specimen of 6-inch cast-iron pipe, two specimens of 3-inch cast iron, and two specimens of 3-inch steel pipe, all 6 inches long. There were also removed from each soil two specimens each of wrought iron, of cast iron, and of open-hearth iron, 12 inches long with external diameters of approximately 1.9 inches, and two 10-inch lengths of 2-inch open-hearth steel. By treating the two specimens of each material, except the 6-inch cast iron, as a single specimen having twice the area of one, it is possible to compare the pit depths on specimens of different materials and dimensions having approximately the same areas, and to obtain an idea of the accuracy of the method of weighting pit depths which was used in earlier soil-corrosion reports. Columns 2 to 7 of table 10 permit such a comparison.

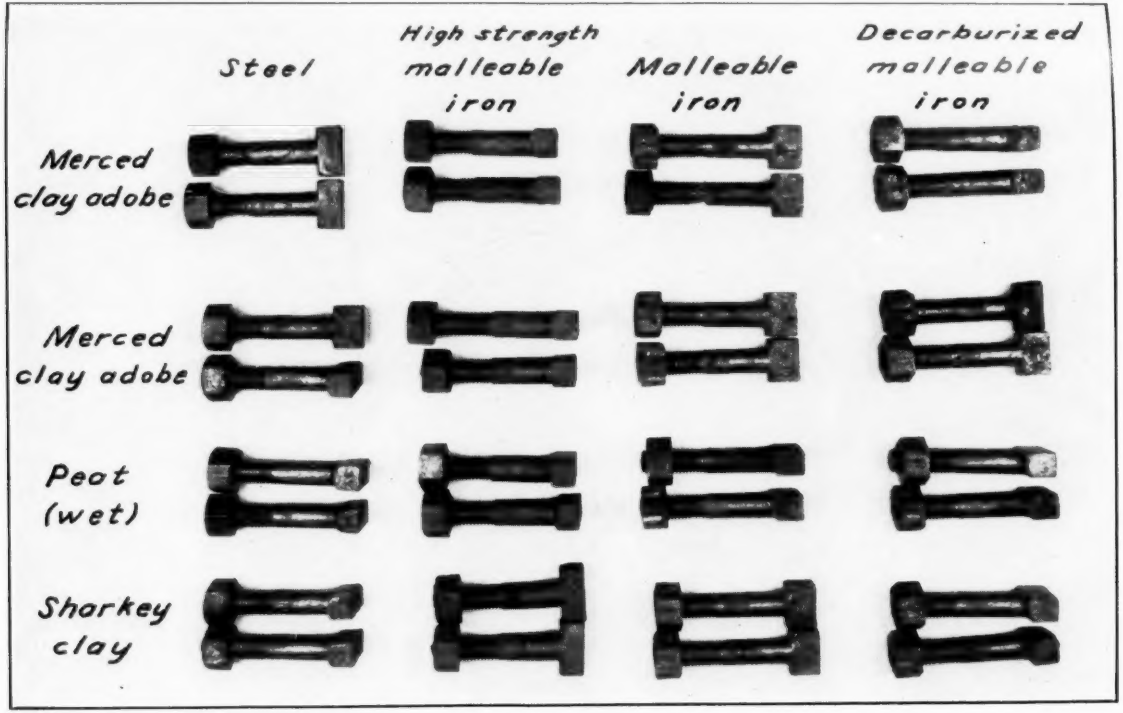

FIGURE 4.—*Appearance of ¾- by ¼-inch bolts after 5 years of exposure in designated soils.*
(The most deeply pitted side of each bolt is shown.)

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TABLE 19.—*Maximum pit depths on pipes of different dimensions*

TABLE 10.—*Maximum pit depths on pipes of different dimensions*

[The total area is approximately the same for all diameters of pipe. All specimens were exposed for approximately 5 years]

Soil [a]	Single maximum pit (mils)							Average of two deepest pits (mils)							Weighted [b] maximum pit depths (mils)			
	Cast iron			Steel		Wrought iron		Cast iron			Steel		Wrought iron		Cast iron			3-in. steel
	6-in.	3-in.	1¼-in.	3-in.	2-in.	1½-in. puddled	1½-in. open hearth	6-in.	3-in.	1¼-in.	3-in.	2-in.	1½-in. puddled	1½-in. open hearth	6-in.	3-in.	1¼-in.	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
51	199	[c] 220	[d] 250+	80	[d] 54+	158	145+	195	[c] 182	250+	72	154+	144	145+	190	[c] 119	250+	55
53	69	56	60	53	53	67	76	65	53	51	52	50	64	65	55	42	44	48
55	37	53	50	91	66	80	96	34	52	51	86	62	78	83	31	44	50	76
56	92	188	127	185	88	67	74	91	178	126	178	82	67	71	78	165	106	171
58	129	132	250+	98	108	79	63	122	129	250+	96	62	68	105	113	109	63	82
59	50	39	36	35	24	25	6	50	38	33	32	5	24	23	45	37	179+	29
60	147	114	68	120	29	47	[c] 34	141	112	68	100	27	43	[c] 32	132	109	31	75
61	65	80	77	60	[c] 85	42	[c] 94	60	76	76	60	[c] 84	41	[c] 88	56	58	53	50
62	41	76	107	61	66	56	98	33	75	107	60	66	56	86	26	62	54	57
63	57	37	107	92	38	25	[c] 81	39	33	77	86	37	24	[c] 57	29	30	88	70
64	222	176	139	144	154+	141	143	220	164	126	125	154+	129	143	203	149	57	100
65	140	189	124	96	79	102	108	139	164	111	87	79	91	103	132	136	113	79
66	165	163	90	217	154+	99	145+	158	163	83	207	154+	94	145+	150	150	82	157
67	138	[c] 198	250+	138	154+	145+	145+	111	194	250+	119	154+	145+	145+	97	[e]	.....	103

[a] See table 1 for the names of the soils and locations of the test sites.

[b] Average of four deepest pits on one 6-inch specimen, and of the two deepest pits on each of two specimens of other diameters.

[c] Individual specimens differed from average by 50 percent or more.

[d] + indicates that one or both specimens were punctured.

[e] Only one specimen of 3-inch cast iron from soil 67.

In 7 of the 14 soils shown in table 10, the 6-inch cast-iron specimens developed shallower maximum pits than were observed on equal areas of 3-inch or 1¼-inch cast specimens, and the average of the maximum pits on the 6-inch specimens is less than the averages for either of the other two sizes of cast-iron pipes. The 3-inch cast specimens developed shallower maximum pits than were found on the 1¼-inch cast specimens in 6 of the 14 soils, and the average of the maximum pits in the 14 soils is slightly greater for the 1¼-inch cast iron. The 3-inch steel specimens developed shallower maximum pits than were observed on the 2-inch steel specimens in 5 of the 13 soils for which comparisons are possible.

Comparisons of specimens of different diameters on the basis of the averages of the two deepest pits yield similar results. The data indicate that when the areas of the specimens are the same, the depth of the maximum pit is not affected by the diameter of the specimen.

In earlier reports the pit depths were weighted to take account of the difference in the areas of the specimens. The depths of the four deepest pits were averaged to obtain the recorded maximum pit depths on the 6-inch cast-iron specimens, whereas the depths of the two deepest pits on each of two 3-inch specimens were averaged to obtain the recorded maximum pit depth on the 3-inch specimens. The 1937 data have been treated in this way to obtain the values in columns 15, 16, and 17 of table 10. In six soils the 6-inch specimens showed deeper weighted maximum pit depths than the 3-inch cast-iron specimens, whereas in six other soils the weighted maximum pit depths on the 6-inch specimens were shallower. The averages of the weighted maximum pit depths for the 3 sizes of cast pipe in 13 soils differ by only 5 mils. It appears, therefore, that the method used in previous reports for adjusting the data on pit depths to take account of the sizes of the specimens has, on the average, produced results that favored neither size of specimen. This was indicated in the earlier papers with respect to wrought specimens by the averages of the weighted rates of penetration for 1½- and 3-inch materials of the same kind, but there remained a question as to whether the pit-depth–area relationship held for cast iron.

8. COMPARISON OF 3-INCH CAST AND WROUGHT SPECIMENS WITH RESPECT TO THEIR DEEPEST PITS

Table 7 shows that in acid soils the 1¼-inch cast specimens developed deeper maximum pits than those found on the 2-inch steel specimens, although the reverse was true in the alkali soils. In table 11, the data of table 10 have been put in a form similar to that of table 7. Table 11 shows no relation between the acidity of the soil and the relative merits of the materials. Neither material in this table appears to be definitely superior to the other with respect to the depth of the deepest pits.

TABLE 11.—*Comparison of specimens of 3-inch cast iron and steel pipe with respect to pitting in acid and alkali soils*

Acid soils			Soils with acidity less than 14 mg-eq per 100 grams of soil			Alkali soils	
Soils in which the deepest pit was on cast iron	Soils in which the deepest pit was on steel	Soils in which the difference was less than 5 mils	Soil in which the deepest pit was on cast iron	Soil in which the deepest pit was on steel	Soil in which the difference was less than 5 mils	Soils in which the deepest pit was on cast iron	Soils in which the deepest pit was on steel
Identification No.	*Identification No.*	*Identification No.*	*Identification No.*	*Identification No.*	*Identification No.*	*Identification No.*	*Identification No.*
58	60	56	51	55	53	64	66
62	63	59	--	61	--	65	--
67	--	--	--	--	--	--	--

9. MATERIALS AT SPECIAL TEST SITES

A number of small sets of specimens have been placed at test sites to afford information to some cooperator or to obtain data on some special corrosion problem. Most of these sets consisted of two specimens of open-hearth iron, wrought iron, Bessemer steel, pit cast iron, and iron cast centrifugally in green-sand molds. All specimens were 6 inches long. The wrought specimens were cut from 3-inch pipe and the cast specimens from 6-inch pipe.

The data from the examination of such specimens removed in 1937 afford another opportunity to study the effect of variations in composition and methods of manufacture on the resistance of commonly used pipe materials to soil corrosion under special conditions. Table 12 shows the losses of weight of the materials in ounces per square foot. It should be noted that the specimens in three of the soils were exposed for approximately 5 years, whereas the others were exposed for about 9 years. Since rates of corrosion vary with the period of exposure, it seemed inadvisable to reduce the data for two periods of exposure to rates of corrosion and to place them in the same table.

It will be noted that some of the soils were much more corrosive than others. No one material lost less weight than any of the others at all of the test sites.

Table 13 shows the maximum pit depths on the different materials. This table differs from some others in that to make the data for the two sizes of specimens comparable, the two specimens of the same wrought material have been treated as one and the single maximum pit on the two recorded in the table.

It will be seen from table 13 that the three wrought materials corroded quite similarly with respect to the depths of the maximum pits. One or more test sites can be found for each wrought material in which that material developed shallower maximum pits than did either of the other wrought materials. It is evident, therefore, that the averages of the maximum pit depths at all of the test sites would have little practical significance since the relative magnitudes of the averages might have been changed if the materials had been exposed to more or fewer soils.

TABLE 12.—*Loss* [a] *of weight of pipe at special test sites*

[In ounces per square foot]

Soil		Duration of test	3-inch wrought materials					6-inch cast iron			
No.	Type		Open-hearth iron	Wrought iron	Bessemer steel	Average	Standard error of average	Pit cast	Centrifugally cast	Average	Standard error of average
		Years									
52	Alkali knoll	5.44	14.7	14.6	13.5	14.3	0.4	25.2	16.2	20.7	3.3
54	Fairmount silt loam	5.25	1.5	1.3	1.2	1.3	.1	2.3	1.6	1.9	.2
68	Gila clay	5.08	3.7	4.3	3.8	3.9	.2	5.3	[b] 4.3	5.0	.5
101	Billings silt loam, low alkali	9.27	10.5	9.4	9.1	9.7	.5	10.6	8.1	9.3	1.0
102	Billings silt loam, moderate alkali	9.27	18.3	16.1	17.6	17.3	.4	25.6	23.1	24.4	2.3
103	Billings silt loam, high alkali	9.27	18.8	21.3	17.8	19.3	.8	50.5	45.2	47.9	5.8
109	Fresno sandy loam, low alkali	9.24	11.7	11.8	11.3	11.6	.4	24.1	21.5	22.3	3.6
110	Fresno sandy loam, moderate alkali	9.24	18.6	15.8	20.2	18.2	1.1	17.8	19.9	18.3	1.8
111	Fresno sandy loam	8.90	17.6	18.8	19.4	18.6	.7	24.8	24.4	24.6	1.0
116	Merced clay	9.27	21.6	19.1	19.4	20.1	.6	40.5	33.4	36.9	3.1
117	Merced clay adobe	9.27	21.0	19.9	20.5	20.4	.4	19.4	15.2	17.3	1.5
120	Panoche clay loam	9.27	5.0	4.5	7.1	5.5	.7	[c] 3.8	3.5	3.6	1.0

[a] Average losses based on 2 specimens of each material except the pit cast iron, of which there was but 1 specimen.
[b] One specimen only; cast in a metal mold.
[c] Losses of individual specimens differed from average by more than 50 percent.

TABLE 13.—*Maximum pit depths on specimens at special test sites*

[In mils]

Soil		Duration of test	Maximum pit on two 3-inch specimens				Standard error of average	Maximum pits on 6-inch specimens				Standard error of average
			Iron		Bessemer steel	Average for all wrought		On one northern pit cast	On one southern pit cast	Average of two centrifugally cast	Average for all cast	
No.	Type [a]		Open hearth	Puddled								
		Years										
52	Alkali knoll [b]	5.44	117	134	129	127	5.8	195	163	168	175	7.3
54	Fairmount silt loam	5.25	15	26	12	18	3.5	36	35	57	43	6.1
68	Gila clay	5.08	45	46	38	43	2.5	93	138	[d] 82	104	14.1
101	Billings silt loam, low alkali	9.27	160	96	94	117	20.8	128	203	165	165	17.7
102	Billings silt loam, moderate alkali	9.27	126	105	95	109	6.9	410	293	247	317	38.7
103	Billings silt loam, high alkali	9.27	213	139	206	186	23.6	418	361	214	331	53.9
109	Fresno sandy loam, low alkali	9.24	125	112	112	116	7.6	269	288	226	249	15.6
110	Fresno sandy loam, moderate alkali	9.24	177	148	189	171	14.3	280	251	277	269	12.7
111	Fresno sandy loam	8.90	[c] 216+	197	153	189+	16.9	265	167	94	175	38.4
116	Merced clay	9.27	124	178	97	133	23.8	270	250	230	250	12.8
117	Merced clay adobe	9.27	200	133	159	164	19.5	204	175	167	182	9.0
122	Panoche clay loam	9.27	59	52	54	55	2.1	90	83	84	86	9.4

[a] See table 1 for locations of test sites and analyses of soils.
[b] In Lake Charles clay.
[c] + indicates specimen punctured.
[d] One specimen only, cast in a metal mold. The other centrifugally cast specimens were cast in sand molds.

The situation is much the same with respect to the three cast materials. No one cast material is superior to both of the other materials in all of the soils. Since the test sites do not represent average soil conditions, the table does not indicate the relative maximum pit depths to be expected on different materials except when the conditions of the tests are duplicated. Although these data seem to show that the pit depths are shallower on wrought materials than on cast materials, the data presented in this and earlier papers indicate that probably the commonly used ferrous pipe materials react similarly with respect to loss of weight and pitting when exposed to similar soil conditions, and in a specific case any one of the materials may show a lower rate of loss of weight or a lower rate of penetration than the others. Such showings may be the result of chance, and it is doubtful whether or not they are of practical importance to the user of underground pipe.

V. NONFERROUS MATERIALS

The dimensions and analyses of the nonferrous pipes buried in 1932 are given in table 14. The specimens were cleaned in dilute sulfuric

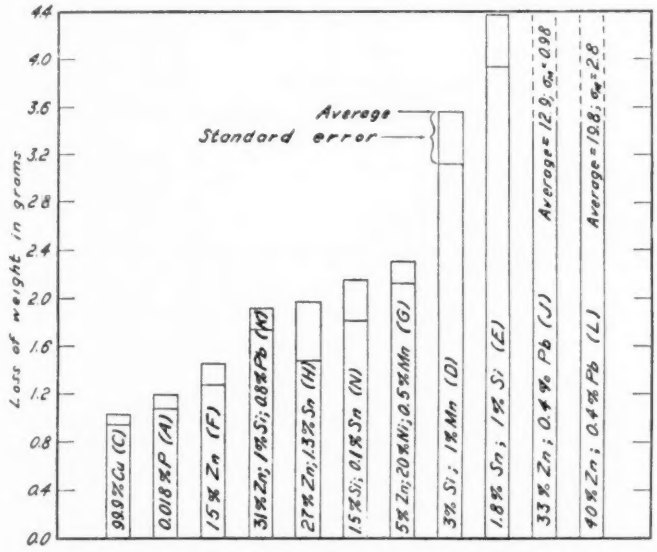

FIGURE 5.—*Losses of weight of nonferrous materials in Merced clay adobe.*

acid and weighed and inspected after cleaning to determine their condition. Table 15 shows the rates of loss of weight for the specimens buried for 5 years and is comparable with table 9 of Research Paper RP945 [2], in which the data for the specimens buried for 2 years are given. Losses of weight are not a fair basis for comparing the corrosion-resistant properties of all alloys of copper. Some of them lose strength more rapidly than weight, because of dezincification. The materials which act in this way are indicated in table 16, although the extent of the dezincification was not determined.

Most of the materials showed rates of loss of weight which are lower for the 5-year period of exposure than for the 2-year period, but in three soils most of the materials showed higher rates of corrosion for the longer periods of exposure. The data are insufficient to show whether or not this apparent tendency is accidental.

Figure 5 permits a comparison of losses of weight of the materials in Merced clay adobe from which a sufficient number of specimens were removed to permit the calculation of the standard errors of the average losses. Whether or not the figure represents the relative resistances of the materials to this soil depends somewhat on the extent of the dezincification of the materials.

TABLE 14.—*Chemical composition of 1.7- by 12-inch nonferrous pipe* [a]

Material		Cu	Zn	Sn	Pb	Ni	Other elements
Symbol	Type						
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
C	Tough pitch copper	99.97					
[b]*A*	Deoxidized copper	99.94					0.018 P.
[c]*M*	Copper with soldered fittings						
F	Red brass	85.18	14.80				.01 Fe.
H	Admiralty metal	71.28	27.39	1.30	0.01		.02 Fe.
K	Two-and-one leaded brass	67.08	31.07		.84		Trace of Fe; 1.01 Si.
J	Brass	66.50	33.06		.42		0.02 Fe.
L	Muntz metal	60.06	39.58		.36		Trace of Fe.
E	Bronze	97.15		1.80			0.01 Fe; 1.04 Si.
[d]*N*	Cu-Si alloy	98.11		[d]1.14		0.01	0.11 Fe; 0.18 Mn; 1.49 Si.
D	do	95.46				.08	0.21 Fe; 1.06 Mn; 3.19 Si.
G	Cu-Ni alloy	74.45	4.99			20.04	0.52 Mn.

[a] Analyses furnished by the pipe manufacturers.
[b] Deoxidized copper, hard temper.
[c] These specimens had streamlined caps and couplings soldered in place.
[d] Some of these specimens had brazed joints.

TABLE 15.—*Rates of loss of weight of nonferrous pipe*

[Ounces per square foot per year]

Soil	Duration of test	Tough-pitch copper	Deoxidized copper	Red brass	Admiralty metal	Two-and-one leaded brass	Brass—66% Cu; 33% Zn	Muntz metal	Bronze—97% Cu; 1% Si; 1.8% Sn	Alloy		
										98% Cu; 1.5% Si	95% Cu; 3% Si	75% Cu; 20% Ni; 5% Zn
		C	*A*	*F*	*H*	*K*	*J*	*L*	*E*	*N*	*D*	*G*
	Years											
51	5.45	0.17	0.19	0.18	0.20	0.066	0.26	0.27	0.19	0.19	0.20	0.16
53	5.46	.029	.028	.030	.038	.060	.041	.055	.051	.045	.046	.027
55	5.20	.037	.027	.043	.049	.047	.065	[a].11	.057	.043	.038	.038
56	5.44	.062	.093	.062	.053	.059	.069	.084	.089	.059	.064	.064
57	5.23	.017	.017	.023	.031	.029	.18	[a].30	.070	.034	.057	.039
58	5.50	.26	.28	.26	.39	.20	.28	.63	.30	.25	.31	.27
59	5.14	.025	.023	.033	.019	.029	.00056	.0042	.054	.042	.019	.028
60	5.25	.89	.73	.78	.68	.57	.98	.84	.72	.79	.63	.68
61	5.50	.061	.064	.069	.11	.10	.18	.32	.092	.077	.095	.061
62	5.47	.047	.047	.049	.066	.10	.10	.22	.11	.073	.078	.057
63	5.55	.54	.44	.097	.020	.027	.0033	.011	.35	.79	.48	.52
64	5.22	.18	.43	.063	.046	.041	.25	1.3	.24	.40	.22	.019
65	[a]5.26	.090	[a].19	.051	.065	[a].19	.22	.30	.14	.10	[a].12	.032
66	5.28	.031	[a].14	.060	.081	[a].16	.17	.32	.097	[a].13	[a].10	.020
67	5.26	1.5	1.77	2.46	2.8	[b]	[b]	[b]	1.071	3.0	4.0	.57

[a] Individual specimens differed by 50 percent or more from average.
[b] Destroyed by corrosion.

TABLE 16.—*Condition* [a] *and rate of maximum penetration of nonferrous pipe*

M=shallow metal attack, roughening of surface but no definite pitting. *P*=definite pitting; rate of pitting less than 1 mil per year. *U*=apparently unaffected by corrosion. *d*=selective corrosion in small spots. *Z*=destroyed by dezincification

Soil		Tough-pitch copper	Deoxidized copper	Red brass	Admiralty metal	Two-and-one leaded brass	Brass—66% Cu; 33% Zn	Muntz metal	Bronze—97% Cu; 1% Si; 1.8% Sn	Alloy		
										98% Cu; 1.5% Si	95% Cu; 3% Si	75% Cu; 20% Ni; 5% Zn
No.	Type	*C*	*A*	*F*	*H*	*K*	*J*	*L*	*E*	*N*	*D*	*G*
51	Acadia clay	*P*	*P*	1.4	*P*	1.3	2.2	1.3	1.4	*P*	2.0	*P*
53	Cecil clay loam	*P*	1.2	1.4	2.4	*P*	2.0	1.1	2.6	1.1	1.8	*P*
55	Hagerstown loam	1.2	1.0	2.1	6.7	*P*	1.9	*Pd*	3.1	1.5	1.9	1.7
56	Lake Charles clay	*P*	*P*	*P*	*M*	*Md*	*P*	*Md*	1.6	*P*	*M*	*Md*
57	Merced clay adobe	1.1	*P*	*P*	*P*	*P*	2.5	[b] 4.2	3.3	*P*	1.0	1.1
58	Muck	2.2	2.2	1.6	5.3	*Pd*	*P*	1.8	6.0	1.3	1.4	1.6
59	Peat	1.2	*P*	*P*	*M*	*M*	*P*	*P*	2.1	*P*	*M*	*P*
60	do	6.3	5.3	4.6	4.8	2.9	6.7	6.4	4.2	3.2	2.9	6.1
61	Sharkey clay	[b] 2.7	[b] 4.2	[b] 3.1	5.8	*P*	2.9	2.4	4.7	2.0	1.2	[b] 2.5
62	Susquehanna clay	1.1	1.6	3.1	3.5	1.6*d*	2.7	1.4	2.7	*P*	1.8	2.7
63	Tidal marsh	*P*	*M*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	2.0
64	Docas clay	1.5	1.7	*P*	1.1	*P*	3.3	3.1	3.6	1.9	2.1	1.1
65	Alkali soil	1.7	1.9	2.5	1.7	1.5	3.0	*M*	4.0	3.0	2.1	*P*
66	Mohave sandy loam	*P*	1.3	1.5	4.7	*P*	1.7	1.5	3.0	[b] 3.4	[b] 2.3*d*	1.5
67	Cinders	10.6	10.2	10.6	16.7	*Z*	*Z*	*Z*	9.3	15.2	17.1	5.5

[a] Averages for 2 specimens for all soils except soil 57, in which 8 specimens have been averaged; figures in mils per year.
[b] Individual specimens differed by 50 percent or more from the average.

The available data do not justify definite conclusions as to the relative merits of most of the nonferrous specimens. However, at all of the test sites copper and its alloys corroded at much lower rates than the commonly used ferrous materials. The pits on many of the specimens were too shallow to be measured accurately by the methods used. The highest rate of corrosion of the nonferrous as well as the ferrous materials occurred in cinders. Copper and the alloys high in copper developed a hard sulfide scale in the tidal marsh, which was removed by scraping.

The specimens of brass, which contained 30 percent or more of zinc, were destroyed by the cinders, site 67.

Next to the cinders, one of the peat soils was the most corrosive. The materials high in zinc showed dezincification in a number of soils.

VI. CEMENT-ASBESTOS PIPE

In 1932 specimens of cement-asbestos flue pipe were included in the test of materials resistant to soil corrosion. Whether or not cement-asbestos water pipe would react to soils in the same way is not known at this time. Specimens of the water pipe were buried at all test sites in 1937.

In view of the questionable significance of the tests of the flue pipe, and because no test of this material has been found which is satisfactory to all interested parties, it seems sufficient to limit the present report on this material to a few general statements concerning the appearance of the specimens.

In the alkali and neutral soils there appeared to be very little change in the specimens. In the acid soils, except the tidal marsh, there was

some softening of the surface of the specimens. It is difficult, if not impossible, to determine to what extent the material was softened, but in most soils it did not appear to be serious. In one very acid soil there was extensive swelling of both ends of both specimens and some cracking of the central section.

VII. NONBITUMINOUS PIPE COATINGS

Eleven varieties of nonbituminous pipe coatings were included in the test of corrosion-resistant materials, but four of these were not placed in all of the soils. Descriptions of these coatings and of their appearance after an exposure of 5 years follow:

Coating *A* was lead with an average thickness of 1.44 mils. In 4 of the 14 soils for which comparisons can be made, one or both of the lead-coated specimens developed deeper pits than were found on the corresponding specimens of unprotected steel pipe. This result may, however, be accidental.

Coating *B* was described as an olefin-polysulfide reaction product. The specimens under observation were made by the addition to this product of small quantities of other materials to form a rubber-like substance. The dimensions of the specimens of this material were 10 by 5 by ¼ inch. They were placed on edge in the trench. At the time the specimens were buried this material could not be satisfactorily applied to a pipe, but there appeared to be a possibility of its use as a pipe coating. It was therefore accepted in the form of sheets. When these were removed in 1937, most of them showed more or less hardening and the surfaces of many specimens cracked when they were bent slightly. This evidence of a change in the material may or may not have a bearing on the use of the material as a pipe coating, since there is usually practically no bending of the coated pipe after it has been placed in the ground.

Coating *C* was a vitreous enamel described by the manufacturer as acid-resisting, free from pinholes. The thickness of the coating was approximately 14 mils. Although tests with a high-voltage, high-frequency apparatus indicated that there were numerous minute points which would allow current to pass, the specimens showed no definite evidence of rust in any of the soils to which they were exposed. There was little or no indication of a change in the coating. Three specimens were pitted; but it seems probable that these pits formed at points where the specimens had been injured.

Coating *D* was described as follows: First coat, 23-percent solution of a rubber derivative in xylene; second and third coats, 30-percent solution of the rubber derivative in xylene; fourth coat, 20-percent solution of the rubber derivative in a mixture of turpentine and mineral spirits. Five percent of the solids was carbon black. The thickness of the coating was approximately 0.010 inch. In most soils the outer layer of the coating was brittle and peeled off readily. In a number of soils the coating blistered and the pipe rusted. In seven soils both specimens bore pits of from 27 to 85 mils.

Coating *E* consisted of two applications of paint which differed in color. Neither the kind of pigment nor the kind of vehicle was specified. The thickness of the coating was approximately 0.005 inch. In most soils this coating blistered and in several of them the coating came off when the soil was removed from the specimens. The pipe

rusted badly in several soils and was punctured in three of them. In all soils, however, the coating definitely reduced corrosion.

Coating *F* was a semiplastic compound, which may be applied cold with a brush, consisting of 4½ parts of treated cashew-nutshell oil, 3 parts of fiber asbestos, and 3½ parts of mineral turpentine substitute. The thickness of the coating was approximately 0.006 inch. Twelve of the specimens of coating *F* were placed in water for 1 week. Pattern tests were then made. All tests indicated pinholes in the coating. On most of the specimens the coating was brittle and many of them contained blisters with rust beneath. In only one soil, however, were the pits on the pipe measurable.

Coating *G* was a hard-rubber compound containing rubber, sulfur, and an accelerator cured to a bone-hard condition. The thickness of the coating was about 0.09 inch. The bond between the pipe and the coating was not strong.

Coating *H* was a highly loaded hard-rubber stock which contained 30 percent of magnesium carbonate and approximately 15 percent of "white substitute." The thickness of this coating was about 0.1 inch.

Coatings *G* and *H* were exposed to six soils. One specimen of coating *G* was cracked in one soil and rust appeared near the end of one specimen in one other soil. Coating *H* completely protected all of the pipe to which it was applied.

Coating *J* was a modified synthetic resin applied to the pipe in the same manner as a paint or varnish. The pipe was then subjected to a baking operation at 425° F for 30 minutes. The thickness of this coating was about 0.002 inch. This coating was removed from only three soils, in one of which it afforded the pipe nearly complete protection.

Coating *K* was a paint coating containing imported highly chlorinated rubber, which may be dissolved in solvents to which may be added drying oils, pigments, quartz meal, or carborundum. The exact ingredients of the coating, which was applied to the pipe 1 inch in outside diameter, were not stated. The coating was applied in Germany. Its thickness was approximately 0.006 inch. The coating was removed from three soils, in all of which the pipe was pitted to a measurable extent but less deeply than were the bare pipes.

Coating *W* was an experimental coating prepared as follows: The pipe was primed with a china-wood oil varnish containing zinc chromate and basic lead chromate. This primer was baked at a temperature of about 200° F for ½ hour. The coating consisted of thoroughly dehydrated china-wood oil to which was added powdered mica and a catalyst. This mixture was molded on the pipe and heated to 200° F for 3 hours. The thickness of this coating was about 0.17 inch.

One or more of the coatings cracked in eight of the soils. The adhesion between the coating and the primer was not good. The primer blistered in several of the soils. Although there was slight rusting of most of the specimens, there was no pitting on any of the specimens, and most of the surface of all of the specimens remain uncorroded. The odor of some of the specimens indicated a change in the material.

Table 17 summarizes the condition of the pipe beneath each coating, except coating *B*, which was not applied to a pipe. In general, it may be said that after 5 years, with the exception of one coating at one test site, all of the coated pipe appeared to be in much better

condition than the uncoated steel pipe in the same soil. However, the brittleness of the thin coatings and the presence of rust beneath them at most of the test sites suggests that they had reached the end of their usefulness in the more corrosive soils.

TABLE 17.—*Condition of coated pipes*

C=Cracked. *D*=Destroyed. *E*=Ends corroded. *H*=Pipe punctured. *M*=Metal attack—pipe roughened by corrosion. *R*=Rusted. *U*=No corrosion. +=Pipe punctured

[Figures indicate depths of maximum pits in mils]

Soil		Specimen number	Pipe coating											
No.	Type		Lead coated	Porcelain enamel	Rubber paint	Paint	Cashew-nut oil-asbestos fiber	Hard rubber	Loaded hard rubber	Synthetic resin	Chlorinated rubber paint	China wood oil-mica compound	Maximum pit on uncoated low-carbon steel pipe
			A	*C*	*D*	*E*	*F*	*G*	*H*	*J*	*K*	*W*	*N*
51	Acadia clay	1	144	*U*	75	53	*M*	.....	.....	.....	.....	*RC*	154+
		2	*H*	*E*	85	65	*M*	.....	.....	.....	.....	*RC*	154+
53	Cecil clay loam	1	37	*U*	*R*	*M*	*R*	.....	.....	*R*	10	*R*	47
		2	37	*U*	*R*	*M*	*R*	.....	.....	*R*	16	*R*	53
55	Hagerstown loam	1	17	*U*	*R*	*M*	*R*	.....	.....	.....	.....	*R*	48
		2	34	.....	*R*	*M*	*R*	.....	.....	.....	.....	*M*	66
56	Lake Charles clay	1	75	*U*	39	*M*	*M*	.....	.....	.....	.....	*RC*	53
		2	37	*E*	27	32	*M*	.....	.....	.....	.....	*RC*	88
57	Merced clay adobe	1	52	19	*M*	*M*	*R*	*U*	*U*	65	29	*RC*	91
		2	55	*U*	27	*M*	*R*	*U*	*U*	43	36	*RC*	100
		3	61	*U*	*M*	*M*	*M*	*U*	*U*	32	25	*R*	140
		4	43	*U*	46	*M*	*R*	*U*	*U*	92	28	*RC*	104
		5	65	*U*	50	*M*	*R*	*U*	*U*	54	21	*R*	104
		6	46	*U*	43	*M*	*M*	*U*	*U*	50	15	*M*	102
		7	31	*U*	39	*M*	*R*	*U*	*U*	41	16	*RC*	55
		8	45	8	26	*M*	*R*	*U*	*U*	48	25	*U*	103
58	Muck	1	63	*U*	*M*	70	*R*	.....	.....	.....	.....	*RC*	97
		2	61	13*E*	*E*	*M*	*R*	.....	.....	.....	.....	*RC*	108
59	Peat	1	*U*	*U*	*U*	*R*	*U*	*U*	*U*	.....	.....	*U*	24
		2	*U*	*U*	*R*	*R*	*U*	*U*	*U*	.....	.....	*R*	15
60	....do	1	78	*U*	57	52	*R*	*U*	*U*	.....	.....	*U*	18
		2	38	*UE*	71	62	*R*	*U*	*U*	.....	.....	*MC*	29
61	Sharkey clay	1	47	*U*	*U*	*M*	*U*	.....	.....	.....	.....	*RC*	23
		2	40	*U*	*U*	*M*	*U*	.....	.....	.....	.....	*U*	85
62	Susquehanna clay	1	75	*U*	*R*	*M*	*R*	.....	.....	.....	.....	*R*	66
		2	34	*U*	*R*	*M*	*R*	.....	.....	.....	.....	*R*	66
63	Tidal marsh	1	*U*	*U*	*U*	*M*	*M*	.....	.....	.....	.....	*MC*	33
		2	*UE*	*U*	*U*	*M*	.....	.....	.....	.....	.....	*MC*	38
64	Docas clay	1	50	*U*	50	*H*	*M*	*U*	*U*	126	.....	*R*	154+
		2	36	*U*	81	*H*	*M*	*U*	*U*	59	.....	*U*	154+
65	Alkali soil	1	61	.....	*M*	75	*R*	*RC*	*U*	.....	.....	*R*	79
		2	60	.....	*M*	70	*R*	*U*	*U*	.....	.....	*U*	69
66	Mohave sandy loam	1	80	31	34	64	*M*	*U*	*U*	.....	.....	*R*	154+
		2	66	*U*	50	*H*	*M*	*U*	*U*	.....	.....	*R*	154+
67	Cinders	1	*D*	*U*	55	*H*	70	*E*	*U*	.....	78	*UC*	84
		2	*D*	*E*	64	88	12	*U*	*U*	.....	.....	*U*	154+
	Thickness of coating, mils	.....	1.4	14	10	5	6	90	100	2	6	170	.....

VIII. SUMMARY

This report is based on the examination of approximately 1,600 specimens of ferrous and nonferrous materials used for underground pipes and protective coatings. The specimens were removed in 1937, after exposures of from 5 to 9 years.

The tables accompanying the paper afford numerous opportunities for the comparison of soils, pipe materials, and pipe coatings; but since

the apparent relative merits of materials may be different for different periods of exposure, it is considered best to defer detailed comparisons of materials until data for longer periods are obtained.

The data do not show many marked differences in the corrodibility of ferrous materials made by different processes. The conditions of the test are unfavorable to the detection of small differences in materials.

The addition of small amounts of chromium, copper, nickel, and some other elements to iron or steel appears to have no marked effect on the resistance of the alloys to soil corrosion.

Ferrous alloys containing large amounts of chromium showed definitely lower rates of loss of weight than the other ferrous materials tested. They also had fewer pits per unit area, but the alloys containing chromium alone were pitted deeply in certain soils.

The addition of nickel to chromium-iron alloys appears to improve the alloy with respect to loss of weight and depth of pits. Tests of alloy sheets indicate that sheets containing 23 percent of chromium, 13 percent of nickel, and 1.8 percent of manganese may be less resistant to soil corrosion than an alloy containing somewhat smaller percentages of these elements.

Two ferrous alloys which contained both copper and nickel in considerable amounts resisted soil corrosion better than the other ferrous materials, with the exception of those containing large percentages of chromium. It is difficult to determine from the available data whether the results should be attributed to one or both of the alloying elements.

Copper and its alloys corroded at much slower rates than the commonly used ferrous materials at most of the test sites. The pits on many of the specimens were too shallow to be measured accurately by the methods used. Dezincification affected the specimens containing large percentages of zinc in several soils.

With one exception, all of the coatings examined appeared to have reduced the intensity and amount of corrosion on the pipes to which they were applied as compared with unprotected pipe. However, many of the coatings showed definite signs of deterioration. A vitreous enamel and two thick rubber coatings afforded almost complete, if not entire protection to all of the specimens to which they were applied. These materials showed no visible signs of deterioration.

The work of cleaning the specimens was done mostly by Melvin Romanoff, W. H. Johnson, and J. A. Brooks. The first two men did most of the work necessary for the preparation of the tables. The author is indebted to I. A. Denison, S. P. Ewing, and several cooperating manufacturers for suggestions as to the significance of the data and the form of the report.

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X-RAY STUDIES OF COMPOUNDS IN THE SYSTEM PbO-SiO_2

By Howard F. McMurdie and Elmer N. Bunting

ABSTRACT

X-ray diffraction powder patterns were made on various compositions in the system PbO-SiO_2 in order to check the presence of certain reported compounds. It was found that three binary compounds exist: $PbO.SiO_2$ (same as the mineral alamosite), $2PbO.SiO_2$, and $4PbO.SiO_2$. The latter occurs in at least two polymorphic forms. The powder patterns of the alpha and beta forms of PbO are also given.

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I. INTRODUCTION

Considerable work has been done by various investigators on the system PbO-SiO_2 [1, 2, 3, 4, 5, 6].[1] These workers agree on the existence of the compounds $2PbO.SiO_2$ and $PbO.SiO_2$. Beyond this there is little agreement. One worker [6] finds the compound $PbO.2SiO_2$. Another [5] suggests the existence of the compounds $3PbO.SiO_2$ and $3PbO.2SiO_2$. The last compound would correspond to the natural mineral barysilite.

Valenkov and Poray-Koshitz [8] studied the system with the X-ray, making powder diffraction patterns of various compositions. They concluded that 3:2, 4:1, and 3:1 compounds did not exist. Mixtures at the 4:1 composition gave, according to them, a pattern of a mixture of βPbO and $2PbO.SiO_2$.

Geller, Creamer, and Bunting [7] investigated the system by thermal studies, optical investigation, and thermal expansion tests, and came to the conclusion that three binary compounds existed: $PbO.SiO_2$ (corresponding to the natural mineral alamosite), $2PbO.SiO_2$, and $4PbO.SiO_2$. The last compound was thought to have three crystal modifications: an alpha form stable above 720° C and melting incongruently at 725° C to PbO and liquid, a beta form stable between 720 and about 140° C, and a gamma form stable below 140° C. The beta to gamma inversion was found to be so rapid that all samples of the beta form which were prepared changed quickly to gamma at room temperature. Heating curves and thermal-expansion measurements indicated the occurrence of the change at 140° C. It was found that the samples of $\alpha 4PbO.SiO_2$ crystallized between 720° and

[1] Figures in brackets indicate the literature references at the end of this paper.

725° C could be quenched successfully to produce the alpha form at room temperature.

The present study was made as a supplement to the work of Geller, Creamer, and Bunting to check by X-ray patterns the compounds found by them.

II. MATERIALS AND METHODS

The samples of the binary compounds were made, using the methods employed in the previous work. The sample of $\alpha 4PbO.SiO_2$ was prepared at 723° C and quenched after holding for 18 hours. The $\gamma 4PbO.SiO_2$ was prepared by first crystallizing the compound for 18 hours at 710° C in the β form and then cooling below 140° C to obtain the γ form. A sample of the natural mineral alamosite was obtained from the United States National Museum, Washington, D. C.

The αPbO (massicotite) was a sample of sublimed "litharge." The βPbO (lithargite)[2] was prepared by precipitation from a hot solution of 15 *N* KOH [9].

The X-ray patterns were made in circular cameras with a radius of approximately 5.70 cm. The samples were mounted on fine glass rods with vaseline and rotated during the exposure period of about 17½ hours. The radiation used was from a gas type copper anticathode X-ray tube, operating at about 45 kv and 4 ma. The β radiation was filtered out with a thin sheet of nickel foil placed over the entrance to the camera slit.

III. RESULTS AND DISCUSSION

The diffraction data obtained on the two forms of PbO, on two forms of $4PbO.SiO_2$, and on $2PbO.SiO_2$ and $PbO.SiO_2$ are given in tables 1 to 6.

TABLE 1.—*Powder diffraction pattern of* α PbO

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	5.89	17	*s*	1.463
2	*ss*	3.01	18	*w*	1.397
3	*m*	2.93	19	*m*	1.366
4	*s*	2.72	20	*m*	1.352
5	*s*	2.35	21	*w*	1.319
6	*ww*	2.26	22	*m*	1.289
7	*ww*	2.19	23	*m*	1.281
8	*s*	1.98	24	*m*	1.241
9	*w*	1.950	25	*m*	1.205
10	*s*	1.830	26	*m*	1.196
11	*s*	1.775	27	*m*	1.181
12	*s*	1.707	28	*m*	1.165
13	*s*	1.595	29	*m*	1.132
14	*w*	1.575	30	*m*	1.113
15	*s*	1.518	31	*s*	1.094
16	*w*	1.508	32	*m*	1.085

[2] E. S. Larsen [14] showed the identity of the two natural minerals of PbO with the two artificial forms. In that article he proposed that "massicot" be used for the tetragonal (β) form and "litharge" for the orthorhombic (α) form. In a later paper [11] he proposed interchanging the names, which conforms to current practice.

TABLE 2.—*Powder diffraction pattern of* β PbO

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	5.07	15	*w*	1.248
2	*ss*	3.10	16	*s*	1.218
3	*m*	2.79	17	*w*	1.193
4	*m*	2.49	18	*m*	1.146
5	*ww*	2.11	19	*w*	1.123
6	*ww*	2.06	20	*w*	1.075
7	*m*	1.97	21	*w*	1.060
8	*s*	1.862	22	*ww*	1.038
9	*s*	1.667	23	*ww*	1.020
10	*s*	1.530	24	*m*	.970
11	*ww*	1.432	25	*w*	.946
12	*w*	1.396	26	*m*	.935
13	*ww*	1.341			
14	*ww*	1.278			

TABLE 3.—*Powder diffraction pattern of* α $4PbO.SiO_2$

[*w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*w*	3.64	13	*m*	2.010
2	*w*	3.36	14	*w*	1.958
3	*ss*	3.10	15	*w*	1.924
4	*s*	3.03	16	*m*	1.891
5	*w*	2.91	17	*w*	1.854
6	*m*	2.83	18	*m*	1.800
7	*m*	2.70	19	*m*	1.790
8	*w*	2.49	20	*m*	1.708
9	*w*	2.31	21	*s*	1.676
10	*w*	2.245	22	*w*	1.635
11	*w*	2.170	23	*w*	1.610
12	*w*	2.120	24	*m*	1.552

TABLE 4.—*Powder diffraction pattern of* γ $4PbO.SiO_2$

[*ww*=very weak; *s*=strong; *ss*=very strong; *w*=weak; *m*=medium]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	3.69	12	*w*	2.02
2	*ww*	3.48	13	*w*	1.958
3	*s*	3.13	14	*m*	1.897
4	*ss*	3.02	15	*m*	1.853
5	*w*	2.93	16	*s*	1.819
6	*w*	2.83	17	*w*	1.730
7	*m*	2.72	18	*w*	1.676
8	*w*	2.65	19	*m*	1.610
9	*w*	2.55	20	*m*	1.563
10	*w*	2.47	21	*m*	1.539
11	*w*	2.31	22	*w*	1.486

TABLE 5.—*Powder diffraction pattern of* $2PbO.SiO_2$

[*m*=medium; *w*=weak; *ss*=very strong; *s*=strong; *ww*=very weak]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*m*	9.80	13	*ww*	2.14
2	*m*	5.97	14	*ww*	2.10
3	*w*	3.71	15	*m*	1.99
4	*w*	3.55			
5	*ss*	3.21	16	*w*	1.93
			17	*m*	1.892
6	*ss*	3.11	18	*m*	1.853
7	*s*	2.98	19	*w*	1.790
8	*s*	2.78	20	*w*	1.750
9	*s*	2.56			
10	*w*	2.44	21	*w*	1.706
			22	*m*	1.653
11	*w*	2.36	23	*s*	1.597
12	*w*	2.22			

TABLE 6.—*Powder diffraction pattern of* $PbO\text{-}SiO_2$ (Alamosite)

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*m*	5.82	11	*w*	2.52
2	*s*	3.58	12	*w*	2.47
3	*s*	3.36	13	*w*	2.34
4	*m*	3.24	14	*m*	2.285
5	*m*	3.02	15	*w*	2.205
6	*w*	2.89	16	*w*	2.135
7	*m*	2.78	17	*ww*	2.080
8	*w*	2.73	18	*ww*	2.050
9	*w*	2.66	19	*w*	2.025
10	*w*	2.59	20	*m*	1.928

The diffraction patterns of the α and β $4PbO.SiO_2$ are similar, but show significant differences. It can be seen that neither of these patterns could be the result of a mixture of β PbO and $2PbO.SiO_2$, as suggested by Valenkov and Poray-Koshitz. Geller and Bunting [16] noted that in mixtures of similar composition, at temperatures considerably below the liquidus, PbO would sometimes crystallize out even though it was not the primary phase. To crystallize $4PbO.SiO_2$ in either form required that the composition be held at temperatures near the top of their stability ranges at least overnight.[3]

Thus, if a melted mixture were cooled before the 4:1 compound formed, PbO and $2PbO.SiO_2$ might result. The modification which was formed would presumably depend on the temperature at which the PbO first crystallized. Therefore, rapid cooling might reduce the temperature of the liquid below that of the α to β PbO inversion before crystallization could take place.

The α to β PbO inversion temperature is not agreed on by investigators. Cohen and Addink [12] report the temperature as 488.5° C. Other values reported are 530° C [13] and 587° C [15].

The entire liquidus curve of this system for compositions in which PbO is the primary phase lies above 725° C. An X-ray pattern of a

[3] After completing this study, we note that Ernst Kordes [17] confirms the existence of $4PbO.SiO_2$. He also prepared $3PbO.2SiO_2$ crystals, but we have done no additional work to obtain it.

mixture of 97.5 percent of PbO and 2.5 percent of SiO_2 held at, and then quenched from, 740° C indicated that α PbO was present.

The inversion from α to β PbO would appear to be very sluggish. Geller, Creamer, and Bunting [7] obtained no breaks in cooling curves made with α PbO. However, the inversion from β to α PbO proceeds rapidly [15].

The α and β PbO patterns check within experimental error the results of the work of Darbyshire [10]. He stated that αPbO (yellow, massicotite) was orthorhombic with $a=5.46$ A, $b=4.72$ A, and $c=3.86$ A. β PbO (red, lithargite) was tetragonal with $a=3.97$ A and $c=5.01$ A.

A diffraction pattern of natural alamosite was also made. While Geller and his coworkers had found the optical properties of prepared $PbO.SiO_2$ very similar to alamosite, the X-ray patterns show conclusively their identity.

IV. SUMMARY

The X-ray examination of compounds in the system PbO-SiO_2 indicates the existence of $PbO.SiO_2$, $2PbO.SiO_2$, and $4PbO.SiO_2$, the last in at least two crystal modifications. The natural mineral alamosite was found to be identical with $PbO.SiO_2$.

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